ELECTRIC BREAKDOWN AND MOISTURE ADSORPTION IN EVAPORATED DIELECTRIC FILMS

by James E.S. Macleod.

Thesis presented

for the Degree of Doctor of Philosophy

in the Faculty of Science of the University of Glasgow.

May, 1965.

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Previous work on evaporated films and on measurement of electric breakdown is reviewed and its relation to the present work is shown. Electric breakdown theory is also briefly reviewed. Results of measurements of the breakdown fields of dielectric films between evaporated metal electrodes are presented. Studies have been made of freshly deposited films in a vacuum which remained unbroken between deposition and testing, and also of films exposed to air saturated with water vapour.

The dielectrics investigated were sodium chloride, lithium fluoride and cryolite (Na_3AlF_6). Sodium chloride was chosen since it has attracted the attention of numerous previous workers so that its breakdown field is well known. Lithium fluoride has not been quite so widely studied, but it is unique among the alkali halides in being only sparingly soluble. This is an important advantage in the work on moist specimens since soluble films tend to disintegrate on exposure to water vapour. Cryolite, another insoluble fluoride, is in common use as a thin film material for optical purposes since it forms films of good stability. If its electrical properties are also suitable it might well be promising as a dielectric for evaporated capacitors. Measurements of its

electrical breakdown could therefore prove useful for practical reasons.

The breakdown fields were an order of magnitude lower than would be expected on the basis of published values for single crystals of the materials. This is in accordance with the results of preliminary measurements made by Weaver in the undernoted Department. It is shown that non-intrinsic breakdown and other unwanted effects are unlikely to have occurred. The low values are attributed to the disordered structure of dielectric films. Possible types of disorder that might reduce the intrinsic breakdown field rather than increase it as observed by Cooper and his colleagues are considered.

It was found that the breakdown field increased with decreasing specimen thickness. This and other aspects of the results suggest an avalanche breakdown mechanism, but reasons are given why this conclusion cannot be regarded as established. The breakdown field also increased as the time of application of the testing voltage was reduced. Possible explanations in terms of time lags to breakdown or of space charge migration are discussed.

The breakdown fields were lower when the anode was of silver than when it was of gold or aluminium. This may be due to migration of silver positive ions in the strong applied field. No other effects of the electrode metal were detected.

Lithium fluoride was used as the dielectric for the detailed studies of films exposed to moisture. The breakdown fields still increased with decreasing thickness but were always greater in magnitude than when the films were tested in an unbroken vacuum immediately after deposition, although still remaining lower than the bulk values. The final breakdown field was greater when the dielectrics were tested while still in an environment of water vapour than

when virtually all moisture was removed before the test by drying in vacuum. Three possible explanations of the rise in breakdown field could be broadly distinguished: (a) adsorbed moisture is solely responsible, more being prese on the films tested under moist conditions than on those dried in vacuum but some water molecules still remaining on the latter films, or (b) the increase in breakdown field of the specimens dried in vacuum is due to recrystallisati and only the further increase in the specimens tested in the presence of mois is directly due to adsorbed layers, or (c) the increase is entirely due to a recrystallisation process modified in some way by the simultaneous presence o the moisture and the electric field to give the further increase in the speci tested under moist conditions. Experiments were therefore performed in which the films were exposed to a field just below the breakdown value while still their environment of water vapour but in which the actual test took place aft drying in vacuum. The results were similar to those for the specimens tested while still in moist air. This is in general consistent only with explanation (c).

Some indications were obtained that the breakdown field increases o exposure to moisture for cryolite and sodium chloride as well as lithium fluo

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CONTENTS

PREFACE

The experimental work described in this thesis was conducted in the Department of Natural Philosophy, Royal College of Science and Technology, Glasgow (now the University of Strathclyde). The author was a Research Student in the Department during the early stages of the work, and later became a Research Assistant under Ministry of Aviation Contract No. PD/65/01.

Dr. C. Weaver, of the above Department, initially suggested the problem, and the research was carried out under the direct supervision of Dr. Weaver, who assisted by discussion and comment at every stage. Otherwise this thesis, the experiments described in it, and the interpretation of the results are the author's original work. Specific exceptions are referred to in the following paragraphs.

The project arose from some observations made by Dr. Weaver, who in the course of his measurements on the capacitances and loss tangents of evaporated dielectric films found that the breakdown fields of the films seemed to be unduly low. A principal aim of the present work has been to investigate reasons for the low values. It was also hoped to obtain information on the breakdown mechanism. Dr. Weaver had found that adsorbed moisture had a profound effect on the capacitances and losses of the films and there were indications of a similar effect on the breakdown fields. In the present work the effects of moisture on the breakdown of evaporated films/

films have been investigated in more detail.

There has been considerable industrial interest in breakdown of evaporated films in recent years. Most of the industrial work has however been directly aimed at the development of thin-film capacitors, and the present work appears to be the only attempt at a more fundamental study since the investigation reported by Plessner in 1948. Plessner used a sphere-and-plane electrode system, which was presumably not intended as a practical configuration for a capacitor. Evaporated metal electrodes were used in the present investigation, which is therefore perhaps the first systematic study of thin-film breakdown under conditions such as might be found in an evaporated capacitor.

The major part of Chapters 1 and 2 consists of a review of previous experimental and theoretical work respectively and by its nature is largely drawn from earlier papers, to which reference is made in the text. Many of the references are drawn from the review articles by Stratton on breakdown theory and by Cooper on breakdown measurements. The presentation of the material and the comments on previous work, however, are entirely due to the author except where it is stated otherwise in the text. In particular the author is solely responsible for drawing attention to the following points: the confusion resulting from the lack of precise knowledge of the refractive index of cryolite (Sub-section 1.2.4); the/

the difficulty in interpreting results on effects of space charge on breakdown fields purely in terms of distortion of the internal field in the dielectric (Sub-section 1.3.1); and the possible counter-criticisms of Vorob'ev's objections to Cooper's suggestion that disorder in an alkali halide monocrystal leads to an increased breakdown field (Sub-section 1.3.2). It is believed that these comments have not been made previously. The fact that the avalanche breakdown field may be insensitive to the critical avalanche size was briefly mentioned by Stratton, but the present author is responsible for the detailed discussion of this point (Section 2.2). The possibility that the discrepancy between different published values of statistical time lag may be due to the different overvoltages used by different authors emerges from Cooper's review article, but this suggestion has also been elaborated by the present author (Sub-section 1.3.3).

The dielectrics studied were lithium fluoride, sodium chloride, and cryolite (Na_3AlF_6). These materials were chosen by the author and Dr. Weaver in consultation. Reasons for the choice are given in Section 1.5.

Chapter 3 deals with the apparatus and techniques used in the investigation. The vacuum pumping unit was built by technical staff according to a standard design in use in the Department. The design of the apparatus in the vacuum chamber was partly based on the standard practice of the Department and partly decided on by/

by the author. The design that is described in this chapter is the one finally adopted after preliminary experiments. Dr. Weaver suggested the use of several specimens on a single slide to speed up the rate of obtaining results.

The circuit of the pulse generator is based on one given by Plessner. The pulse generator and the apparatus in the vacuum chamber were constructed by the author with the assistance of the departmental technical staff. Standard techniques were used for evaporating the films and for measuring their thicknesses.

The experimental work was carried out entirely by the author. Chapter 4 is a report of the results for freshly deposited specimens tested in vacuum. The method of determining the breakdown voltages was developed by the author in the course of preliminary investigations, of which some important aspects are discussed in Section 4.1. At this stage serious difficulty was encountered since specimens were frequently short-circuited. Messrs. J.H. Bruce and J.R. Balmer, of the Ministry of Aviation, pointed out that this might be due to the use of silver electrodes since previous workers had had difficulty with this metal. Electrode effects were subsequently studied in some detail (Section 4.2) and the results seem to indicate that silver behaves anomalously as an anode metal. This appears to be the first time that such effects of silver have been noticed with voltage application times as short as those used here (typically of the order of 10 milliseconds). Dr. Weaver

suggested/

suggested that the behaviour of silver anodes might be due to migration of Ag^+ ions in the strong applied field. The author has attempted (Section 4.2) to elaborate on this suggestion but has been hampered by the lack of quantitative data on this property of silver.

The principal aspects of the results for freshly deposited specimens are presented in Sections 4.3 and 4.4. The low values of breakdown field were confirmed, and the breakdown field was found to decrease with increasing specimen thickness and with increasing applied voltage duration.

Chapter 5 is devoted to the results of tests on lithium fluoride specimens exposed to saturated water vapour. Effects of moisture on insulation failure have been widely studied, but mainly in connection with non-intrinsic mechanisms. An effect was noticed by Plessner, but with his electrode system moisture led to a reduced breakdown field. In the present work the first observation was that when a lithium fluoride specimen was allowed to adsorb moisture to saturation and then tested while still in its moist environment the breakdown field was greater than for a freshly deposited film of the same thickness tested in vacuum. No such effect seems to have been noticed before and the present investigation of moisture effects is apparently entirely new. Messrs. Bruce and Balmer requested the work on specimens exposed to moisture and then dried by being kept in vacuum before being tested/

tested, and this series of experiments yielded the interesting result that the breakdown field was intermediate between the "freshly deposited" value and the value for specimens tested in moist air. This led the author to suggest that the observed effects of water vapour were due to some combination of recrystallisation of the specimen and direct effects of the adsorbed layers (Section 7.3). Dr. Weaver suggested the method of distinguishing these effects by applying a voltage to a specimen in the presence of moisture and then testing after drying the specimen in vacuum. The results of this work strongly suggest that the increase in breakdown field is almost entirely due to recrystallisation, moisture having little or no direct effect.

Most aspects of the interpretation are discussed in Chapter 6. Sections 6.1 to 6.3 deal with the possibility of non-intrinsic mechanisms and other extraneous effects that might have affected the results. These sections are due entirely to the author. The main points of interpretation are in Sections 6.9 to 6.11 which occupy more than half the length of the chapter. Dr. Weaver pointed out the tendency of the dependence of breakdown field on thickness to suggest an avalanche breakdown mechanism, and the possible explanation of the low breakdown fields in terms of voids. The detailed discussion of these points is mainly due to the author, who is also responsible for the other main suggestions including the alternative/

alternative interpretation of the low breakdown fields in terms of electronic or ionic space charge migration possibly involving vacancy clusters, the discussion of possible explanations of the dependence of breakdown field on applied pulse duration, and the suggested explanations of the effects of moisture.

The first four sections of Chapter 7 contain practically no new material, but form a summary of the principal conclusions. This is followed by some suggestions for further work (Section 7.5). The use of films deposited on heated substrates was suggested by Dr. Weaver. The author suggested the testing of epitaxially grown films, the direct measurement of time lags, and the further study of aging including aging under moist conditions with its possible practical applications.

ACKNOWLEDGMENTS

Thanks are due to Professor J. Irving of the Department of Natural Philosophy, University of Strathclyde, for provision of research facilities. Grateful acknowledgment is also amde of the interest taken in the author's work by Professor Irving, by his staff and research students, and by his predecessor, the Late Professor J.S. Rankin.

The author has particular pleasure in thanking Dr. G. Weaver, Senior Lecturer in Natural Philosophy, for many helpful comments and suggestions. Dr. Weaver suggested the research problem and has shown a continuing interest throughout the progress of the work described in this thesis.

Acknowledgment is made to Messrs J.H. Bruce and J.R. Dalmer, of the Ministry of Aviation, for helpful discussions.

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ELECTRIC BREAKDOWN AND MOISTURE ADSORPTION IN EVAPORATED DIELECTRIC FILMS.

CHAPTER 1

INTRODUCTION.

1.1 Electric Breakdown of Thin Films.

The optical properties of vacuum-deposited dielectric layers have been studied for many years (Heavens 1955, 1960). More recently their electrical properties, including their electric breakdown fields, have come under investigation as interest has arisen in the development of thin-film capacitors. Much of the experimental work on electric breakdown of dielectric layers has so far been concerned with materials that are immediately suitable for use in evaporated capacitors, such as silicon oxide (cf. Siddall 1959 - 60), and future progress could well be influenced by a more general investigation.

The electrical breakdown of thin specimens is also of theoretical interest. When a solid insulator breaks down under the influence of an electric field any of several different mechanisms may be at work. Some of these mechanisms involve processes extraneous to the dielectric: the insulating material may have had its stability reduced by chemical action, or a discharge may have taken place in the ambient medium near the surface of the insulator and so caused the insulator itself to be disrupted (Whitehead 1951, Mason 1959). Alternatively the dielectric may be disrupted mechanically by the electrostatic force between the electrodes (Mason 1959).

There also exist mechanisms involving processes that take place/

place in the solid dielectric itself. These are conventionally divided into two main classes: "thermal" breakdown, in which the solid is heated by electrical conduction currents until it reaches a temperature at which it is disrupted (Whitehead 1951), and "intrinsic" breakdown (also known as "electronic" or "purely electric" breakdown), a broad heading including a number of mechanisms in which breakdown is brought about by a catastrophic increase in the total energy of free electrons. Various ways of freeing these electrons are postulated in the different intrinsic breakdown theories. In "field-emission" breakdown the electrons are assumed to be emitted from potential wells (Zener effect) when a field approaching the breakdown value is applied. In "collective" breakdown the electrons are freed by thermal vibration of the lattice. In "avalanche" breakdown electrons are liberated by ionising collisions of existing free electrons with lattice ions; the starting electrons may be thermal or may be freed by internal field emission (Zener effect) or by external field emission from the cathode if the latter is of metal.

These mechanisms may be distinguished in experimental work by certain characteristics predicted by the theories. In particular avalanche breakdown differs from the other mechanisms in that the breakdown field decreases with increasing thickness, in that the breakdown voltage cannot be less than the appropriate ionisation potential of the lattice ions, and in that a statistical time lag, decreasing/

decreasing with increasing overvoltage, exists as an essential feature of the mechanism. Breakdown theories are surveyed in more detail in Chapter 2.

In engineering practice the extraneous mechanisms are probably responsible for the majority of insulation failures, particularly when the ambient medium is moist air. Thermal breakdown is also of considerable technical importance. The importance of the intrinsic mechanisms, on the other hand, usually lies rather in the fact that studying them may lead to increased understanding of the solid state.

However in a very thin dielectricspecimen the length of any available conducting path between the electrodes through the ambient medium may be unfavourable for the development of a gaseous discharge, and the small thickness will facilitate rapid loss of any heat generated by conduction currents so that thermal breakdown is relatively unlikely to occur. Thus if breakdown takes place the probability of an intrinsic mechanism is comparatively high. Moreover the decrease in breakdown field with increasing specimen thickness predicted by the theory of avalanche breakdown becomes strong when the specimen thickness is small. Thus the results of measurements on breakdown of thin films may provide a means of distinguishing between different intrinsic mechanisms. One must however bear in mind that, in the case of an evaporated film, the thickness dependence of the breakdown field may be affected by the complicated structure (Section 1.2). Breakdown studies of evaporated layers may therefore be more useful in revealing any effects of this kind.

In/

In spite of the above considerations the literature on breakdown measurements of thin specimens is meagre in comparison with that on bulk breakdown. Most of such papers as do exist (Sub-section 1.3.5) are concerned with cleaved sheets of mica and with anodised alumina layers, although some authors have studied the thickness dependence of the breakdown field in monocrystalline specimens of alkali halides notwithstanding the difficulty of obtaining thin enough samples for the variation to be appreciable. In evaporated films the investigation by Plessner (1948) is almost the only one so far carried out. Plessner studied films of calcium fluoride, sodium fluoride, and potassium bromide. The electrodes were a silver film deposited before the dielectric and a steel ball-bearing held against the dielectric surface with a force estimated at 10 dynes. The testing voltage was applied in the form of a single sawtooth pulse of the shape sketched in Fig.3.1 (inset). The breakdown fields in general increased with decreasing film thickness in the range 250 Å to 10,000 Å. This is in qualitative agreement with avalanche breakdown theory. However results for each material were obtained only at three or four film thicknesses and it is not possible to compare the form of the dependence with the theoretical equations (Section 2.2) as is done in Sub-section 1.3.5 for previous results on systems other than evaporated films. Plessner also found that the breakdown fields decreased as the duration of the applied pulse was increased from about/

about 10^{-6} sec to 10 sec. Only tentative explanations could be put forward at the time, but later work has suggested that a variation of this type may result from space charge migration in the dielectric (Sub-section 1.3.1) or from the existence of a time lag to breakdown (Sub-section 1.3.3).

Siddall (1959 - 60) studied the dielectric properties and electrical breakdown of silicon oxide films between evaporated aluminium electrodes. It was found that when breakdown took place the electrode metal vaporised locally in the region of the conducting path formed, so that the specimen was once again open-circuited. This "self-healing" effect permitted gross defects to be burnt out and also facilitated measurement of the breakdown strength since repeated breakdowns could be observed on a single specimen. To compare the behaviour of films evaporated under different conditions, a d.c. voltage increasing in steps of 12 volts was applied and the number of breakdown pulses occurring in 30 seconds was counted at each value of applied voltage. Typically no pulses were observed until a critical applied voltage was reached. Thereafter the number of pulses first increased slowly with further increase in voltage, and then increased fairly abruptly when the applied voltage exceeded a further critical value. Since the essential aim of Siddall's work was to develop suitable evaporation techniques for producing capacitors, no attempt was made to identify any absolute value of breakdown field.

Weaver/

Weaver (1962), during his measurements of the capacitances and loss tangents of dielectric films between evaporated metal electrodes (Section 1.2) noticed that the voltage that could be applied to a specimen before it broke down and short-circuited seemed unduly small. The low values were apparently not merely due to thin spots in the dielectric films (Section 6.3). Weaver also observed that adsorbed moisture strongly affected the capacitances and losses of the films, and there seemed to be a similar effect on their breakdown fields.

The low values of breakdown field may be associated with the film structure. Existing information on the structure of thin dielectric films is reviewed in the next section. Measurements of dielectric properties are also discussed since they are closely related to the structure and since they may give information on electronic processes of importance in the breakdown of the films. Section 1.3 is a general review of previous work on electric breakdown, mainly in single crystals of alkali halides.

1.2 Structure and Dielectric Properties of Thin Films.

1.2.1 Dielectric properties of thin films. Weaver (1962) made an extensive investigation of the capacitances and loss tangents of films of MgF_2, CaF_2, LiF, NaF, NaCl, NaBr, KBr, RbBr, and ZnS, sandwiched between evaporated silver electrodes. Both tan δ and the capacitance showed a strong aging effect in most of these dielectrics. The details of the aging process varied from substance/

substance to substance, but tan δ usually exhibited initially high values which decreased with time. The capacitances showed a similar but less strong tendency. It is known that the vacancy concentration, in a freshly deposited film, exceeds the thermodynamic equilibrium concentration, and that excess vacancies diffuse out over a period typically of the order of hours at room temperature (Seitz 1946). Weaver showed that the initially high values were due to space charge polarisation associated with cation vacancy migration and that the decrease in capacitance and tan δ took place as the vacancies diffused thermally out of the film.

Exposing a film to dry air had no effect, but exposure to atmospheric air resulted in pronounced and rapid increases in capacitance and tan δ. In insoluble dielectrics the effects of moisture were completely reversible. When the vacuum chamber, with the specimen in it, was re-evacuated, tan δ and the capacitance returned to the values they had before admission of moist air.

Weaver's results for dielectrics in the absence of moisture had suggested that there were loss peaks at very low frequencies. Confirmation was obtained by Macfarlane (1964) who observed peaks at frequencies down to about 0.01 c/s and in some cases obtained results suggesting peaks at still lower frequencies. Macfarlane's results strongly suggested space-charge polarisation due to migration of vacancies through the whole thickness of the dielectric as the principal loss mechanism giving these very low-frequency peaks. However smaller peaks were observed at frequencies about two orders of magnitude greater, showing the existence of a subsidiary mechanism/

with a shorter relaxation time. This mechanism appeared to be migration of vacancies across the thickness of individual crystallites with blocking at grain boundaries. Macfarlane suggested that the blocking would be only partial, thus explaining why both mechanisms can operate simultaneously.

1.2.2 Structure of thin films. Several methods are available for studying the structure of thin films. The crystallinity (crystallite size, orientation) may be investigated by electron diffraction. The electron microscope gives more direct information on the crystallite size and the general appearance of the film surface. With very thin films transmission electron micrographs can be obtained, and in recent years the technique of evaporation within the microscope has facilitated studies of the early stages of film growth (Blackburn and Campbell 1963, Mullen 1964). With thicker specimens replica techniques must be used.

Thin films of many substances are known to contain voids (cf. Heavens and Smith 1957). The porosity of a film may be determined by measuring the mean density, provided the density of the bulk material is known. Several optical methods for porosity measurement have also been developed; if they are used it is necessary to know the bulk refractive index.

References on results obtained by these techniques are given in the following sub-sections, which deal with the particular dielectrics investigated in the present work. Reasons for choosing these/

these materials are given in Section 1.5.

1.2.3 Lithium fluoride films. Weaver found that in lithium fluoride the initial values of the loss tangent exceeded the bulk values by only about one order of magnitude, whereas in the other alkali halides the losses were greater by about two orders of magnitude. Lithium fluoride was also unusual in that no change in tan δ was observable on aging for periods up to about two weeks. These observations were attributed to the relatively high energy of vacancy formation in lithium fluoride which will lead to a correspondingly low concentration of vacancies. The effects of moisture were completely reversible in lithium fluoride as in other insoluble dielectrics.

The structure of evaporated lithium fluoride films has been fairly extensively studied. Schulz (1949) investigated its properties by several methods. Electron diffraction work revealed a microcrystalline structure. At thicknesses below 100 Å the films had a [100] fibre orientation which was interpreted as being due to a tendency for crystallites about 50 Å on edge to rest on their cube faces. With increasing thicknesses the orientation became random, but a tendency to [111] orientation developed at about 600 Å and became stronger with further increase in thickness. Electron micrographs of thick films seemed to confirm this observation by showing cube-shaped crystallites with their body diagonals roughly perpendicular to the substrate. The crystallite size/

size increased with the film thickness, an average crystallite being about 750 Å on edge in a film 70 000 Å thick. However Schulz reported that it was difficult to obtain clear micrographs because of a tendency for replica material to run into accessible voids when in solution, so that the final replica was distorted on being separated from the lithium fluoride film.

The existence of voids was also shown by measuring the refractive indices of the films by a total reflection technique. In this case voids which were inaccessible to the contact liquid could be detected as well as those which were accessible. The concentration of inaccessible voids increased from 0 to 3.1% and that of accessible voids decreased from 30% to about 15% as the specimen thickness was increased from 20 000 Å to 180 000 Å.

Halliday et al. (1954) concluded from an electron diffraction study that lithium fluoride films exhibited [100] fibre orientation even at large thicknesses, while Bauer (1956) found that a [100] orientation in thin films became random as the thickness increased. Thus Schulz's observations were not confirmed. Bauer did observe a [111] orientation in thicker films, but only when the dielectric vapour was obliquely incident. Bauer's results suggested that the average crystallite size was about 1000 Å.

It is now well known that lithium fluoride films are in tensile stress. Blackburn and Campbell (1963) studied the stress as a function of film thickness and deposition rate by measuring the deflection./

deflection of a glass cantilever with the film deposited on it. After an initial rapid aging which was attributed to temperature gradients across the film thickness, the stress increased more slowly to a final steady value. It was suggested that the cause of the stress might be either diffusion out of the film of excess vacancies produced during deposition (Hoffman et al. 1954) or anomalous lattice spacing in the crystallites (cf. Halliday et al. 1954).

In films exposed to water vapour, or in films of thickness greater than about 10 000 Å aged under dry conditions, the tensile stress is relieved by crazing. Mullen (1964) showed that crazing in the presence of moisture is closely associated with recrystallisation of the film material. A carbon replica technique was used. (Carbon replicas are made by evaporating a carbon film about 40 Å thick over the specimen in vacuum. The specimen need not necessarily be exposed to the atmosphere before the replica is made. In studying evaporated films this is an important advantage over other replica techniques.) Freshly deposited specimens had a very fine structure over most of their area, but there were some crystallites about 500 Å on edge. When exposed to atmospheric air a lithium fluoride film recrystallised in less than a second, and an electron micrograph showed that the film was now entirely composed of crystallites rather more than 500 Å on edge. The process cannot be due to solution in view of the small amount of water vapour available and the/

the low solubility of lithium fluoride, and it was suggested that the dipole fields of the strongly polar water molecules on the film surface modify the lattice binding forces in such a way as to allow movements at grain boundaries. It is difficult to deduce the orientation from the micrographs of freshly deposited films, but those of films exposed to moisture suggest a [111] fibre orientation.

Summary. Lithium fluoride films are microcrystalline. The crystallite size depends on the film thickness and is affected by moisture but is an appreciable fraction (about 0.1 to 0.5) of the film thickness. Disagreement exists as to the crystal orientation but films more than a few hundred Å thick seem to show fibre orientation, probably with the [111] axis normal to the substrate. The films are porous with a void content typically between 20% and 30%. Electrically, lithium fluoride films behave like films of other dielectrics except that their loss tangents have low initial values and change only relatively slowly on aging.

1.2.4 Cryolite films. Macfarlane showed that the dielectric properties of cryolite in thin film form are similar to those of the alkali halides.

Heavens and Smith (1957) state that cryolite films have a void content of not more than about 10% unless the dielectric vapour is obliquely incident on the substrate during deposition. However different authors disagree as to the porosity of cryolite films. The/

The confused picture is probably at least partly due to the uncertainty surrounding the refractive index n_{cry} of bulk cryolite. Few workers on cryolite films have measured n_{cry} themselves and the previous values they assumed do not agree.

Bourg (1962, 1963), using an optical method, found that the porosity of cryolite films decreased with increasing substrate temperature and with improving vacuum but was never less than about 7%, even at 100°C and at pressures of the order of 10^{-6} torr. However the relatively high value of 1.365 was assumed for n_{cry}, and the calculated void content would have been less if a lower value had been used.

Schulz and Scheibner (1950) were able to fit the experimental results of optical measurements closely to a theoretical curve provided they assumed $n_{cry} = 1.34$. The method seems to have been sensitive to about the second decimal place, and hence by applying the Lorentz - Lorenz formula

$$\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2} = \left(1 - \frac{p}{100}\right) \frac{n_{cry}^2 - 1}{n_{cry}^2 + 2}$$

where $\bar{n}$ is the mean refractive index of the film and p is the percent porosity, one can deduce that values of p greater than about 2% could have been detected. The results thus seem to indicate a practically continuous film, but again the uncertainty as to the value of n_{cry} renders the conclusion doubtful.

In an extensive investigation, Koppelmann et al. (1961) assumed/

assumed $n_{cry} = 1.338$. $\bar{n}$ was less than this value in films of thickness 3000 Å to 5000 Å, but greater in 1200 Å films. To explain the high values the authors suggest that compounds of AlF_3 and NaF other than pure cryolite were being formed. It is also possible, however, that the assumed value of n_{cry} has been too low. The mean porosity calculated from the measured refractive indices of the thicker films is 5% whereas the authors obtained values of about 10% by density measurements, and the fact that the calculated porosity is lower than that measured directly again tends to indicate that the bulk refractive index was higher than assumed. Unfortunately the densities of the thinner films were not determined.

The results of reflectivity measurements suggested the existence at the film-air interface of a transition layer whose refractive index may be either greater or less than that of the main part of the film. The value assumed for n_{cry} affects the magnitude of the refractive indices of the two parts of the film but not the conclusion that a transition layer exists. Results tending to indicate a "couche de passage" were also obtained by Bousquet (1955).

Koppelmann et al. also found that the effect of exposing a cryolite film to air saturated with moisture was to produce a partly reversible increase in refractive index. On repeatedly admitting moist air and re-evacuating, the refractive index rose and/

and fell through the reversible part of the increase.

1.2.5 Sodium chloride films. The results of Weaver and of Macfarlane show that the dielectric properties of sodium chloride films do not differ in any important respect from those of a typical dielectric film as described in Sub-section 1.2.1.

Sodium chloride, in common with other soluble alkali halides, has been rather neglected as regards structural investigations. Schulz (1949) studied evaporated sodium chloride by electron diffraction and electron microscopy. As the film thickness increased the orientation followed the sequence [100] - random - [110] - random or slight [210], the first transition taking place at about 100 Å and the last at about 25 000 Å. On exposure to moist air recrystallisation was detected by observing the diffraction pattern. Micrographs were given only for very thin films that had been exposed to the atmosphere.

Ramos and Wilman (1962) also made an electron diffraction study and found the orientation sequence random - [111] - [211], the first transition taking place about 1000 Å and the second at about 10 000 Å. Possibly an initial [100] orientation was not observed since it occurred only in very thin films. At greater thicknesses the [111] orientation recorded by Ramos and Wilman was found by Schulz only in films condensed from vapour that had been reflected from some surface inside the vacuum chamber before striking the substrate.

Schulz/

Schulz gave electron micrographs showing recrystallisation of very thin sodium chloride films on exposure to moisture. No similar study for thicker films of this material has been seen. However Weaver (1962) published optical micrographs showing that rubidium bromide films recrystallised on exposure to water vapour to form cube-shaped crystallites about 0.01 mm (100,000 Å) on edge. This tends to imply that the film was no longer continuous. Sodium chloride has a lower solubility than rubidium bromide, but one would expect similar although less drastic recrystallisation.

1.3 Previous Experimental Work on Electric Breakdown.

In interpreting any experimental results on electrical breakdown of solids, the possibility of effects due to space charge migration and to the structure of the dielectric must be taken into account. These effects are discussed in the first two of the following sub-sections. In the remainder of this section recent work giving information on the breakdown mechanism is surveyed. Most of this work has been concerned with single crystals of alkali halides, but other solids are referred to from time to time.

The earlier work on electric breakdown is not discussed here. For a full review the reader is referred to the book by Whitehead (1951).

1.3.1 Space charge effects. A graph given by Cooper (1962), reproduced in Fig.1.1, shows the breakdown fields measured for potassium bromide by various workers as a function of temperature.

The/

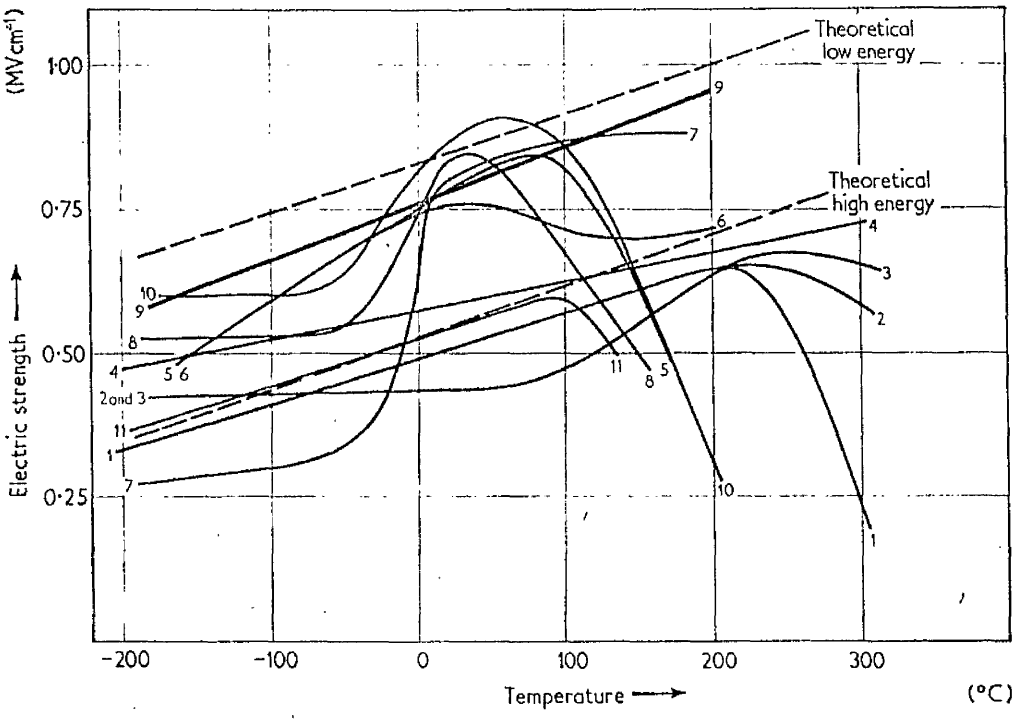


Fig.1.1

Breakdown field of potassium bromide according to various workers, after Cooper (1962).

1. Von Hippel and Alger 1949, d.c.
2. Von Hippel and Alger 1949, 10^{-3} sec single sawtooth.
3. Von Hippel and Alger 1949, 10^{-4} sec single sawtooth.
4. Von Hippel and Alger 1949, 10^{-6} sec single sawtooth.
5. Kuchin 1959, d.c.
6. Kuchin 1959, 10^{-6} sec single (apparently sawtooth).
7. Austen and Whitehead 1940, d.c.
8. Buehl and von Hippel 1939, d.c.
9. Konorova and Sorokina 1957, 10^{-6} sec single.
10. Konorova and Sorokina 1957, d.c.
11. Cooper and Fernandez (Cooper 1962), series, flat-topped.

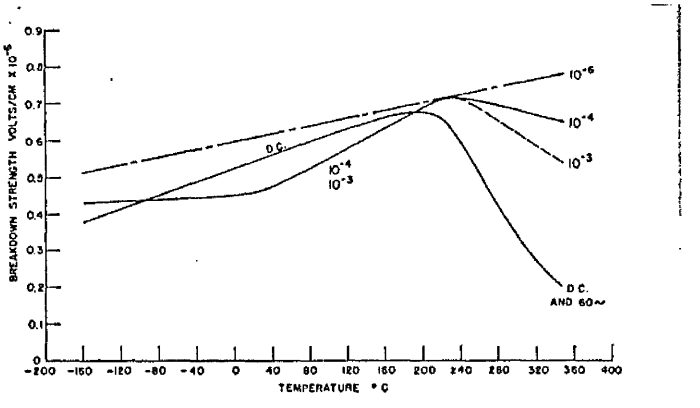


Fig.1.2

Breakdown field of potassium bromide after von Hippel and Alger (1949).

The different sets of results show that when d.c. applied voltages are used the breakdown fields increase to reach a maximum at a critical temperature T_c and then decrease with further increase of temperature. With applied voltage pulses of about 1 microsecond duration, on the other hand, a monotonic increase with temperature is observed and there is no discontinuity at T_c. The difference is more clearly seen in Fig.1.2, which is reproduced from the paper of von Hippel and Alger (1949) and shows these authors' results alone. This diagram also shows that with longer pulse voltages an intermediate situation is found at temperatures above T_c.

The various sets of results in Fig.1.1 disagree seriously as to the values of the breakdown field. For this reason, and since the breakdown fields predicted by different theories do not differ greatly, it is impossible to determine the breakdown mechanism from the graphs. Nor is it easy to account for the decrease in breakdown field with increasing temperature above T_c, for most breakdown theories predict an increase in breakdown field with temperature. An exception is Frohlich's high-temperature theory (Section 2.3), which predicts an exponential decrease in breakdown field with increasing temperature. This theory assumes an electron density in excess of a critical value, and in proposing it Frohlich suggested that this density would be reached at high temperatures. In this way he was able to explain the existence of T_c and other aspects of the observed behaviour. Frohlich's/

Frohlich's suggestion cannot however be reconciled with the fact that at short applied voltage durations the decrease with increasing temperature is not observed and T_c cannot be distinguished.

Von Hippel and Alger (1949) suggested that at high temperatures positive ions might have enough mobility to migrate to the region near the cathode giving a high enough concentration to increase the field locally, so that breakdown would take place at a lower mean applied field. A similar effect may arise from the existence of a negative space charge composed of electrons. The occurrence of related effects has been confirmed elsewhere by von Hippel and his colleagues (von Hippel et al. 1953; cf. von Hippel 1954, pp. 232 et seq.). The ionic mobility may be too low to permit space charge formation when the duration of the testing voltage is very short.

In studying effects believed to be due to space charge migration it is desirable to be able to control the ionic conductivities of the specimens. This may be done in ionic crystals by irradiating them so as to produce F-centres which may then be ionised by illumination. Several authors have used this technique (von Hippel and Alger 1949, Imaishi and Suita 1954, Vorob'ev and Vorob'ev 1958b, Vorob'ev and Kostrygin 1962). In general the breakdown field is depressed in illuminated coloured crystals. This observation is consistent with the suggestion that/

that space charge migration may influence breakdown fields.

An alternative way of increasing the ionic conductivities of alkali halide crystals is to dope them with divalent impurity (Cooper et al. 1960). The additional positive ion vacancies formed in this way are for the most part free from the divalent metal ions, which are themselves relatively immobile, so that positive ion migration is almost the only mechanism contributing to the increase in ionic conductivity (Seitz 1954). When divalent impurity ($PbCl_2$) was added to KCl in concentrations of 0.009 and 0.02 mol % Pb/K, the critical temperature decreased from about + 110°C to about - 60°C and - 120°C respectively, so that the breakdown field was reduced at temperatures above the new critical temperature. When short pulses (0.5:5 μsec) were used the decrease at high temperatures disappeared, in accordance with the results of von Hippel and Alger. Finally the best values of ΔV, the depth of shallow electron traps in Frohlich's high-temperature theory (equation 2.7), were calculated from the results to be of the order of 0.1 eV, whereas one would expect much larger values. These facts together strongly tend to confirm that space charge effects involving positive ions are responsible for the low values of breakdown field at high temperatures rather than Frohlich's high-temperature mechanism.

In pure NaCl tested with 1:5000 μsec pulses the breakdown field was found to decrease very slowly with temperature in the range/

range - 200°C to + 150°C. This is not in agreement with the results of Kuchin (1959) who found that the behaviour of NaCl was qualitatively similar to that already described for KCl. The number of specimens tested seems adequate in both investigations. Possible reasons for the difference are that Cooper et al., unlike Kuchin, used annealed specimens, and that Kuchin used natural rocksalt which would contain unidentified impurities whereas Cooper et al. used crystals grown by the Kyropoulos technique from a melt of analar purity salt. In NaCl crystals containing up to 0.096 mol % Cd/Na of $CdCl_2$ Cooper and his colleagues observed that the only effect doping had on the breakdown field was to increase it at low temperatures.

A difficulty in understanding the effects of space charge in electric breakdown arises from the results, summarised in Subsection 1.2.1, of the dielectric constant and loss measurements made by Weaver (1962) and Macfarlane (1964). The principal polarisation mechanism involved migration across the entire specimen thickness. The frequencies at which the associated loss peaks occurred were seldom greater than 100 c/s even at temperatures in the region of 150°C, and were often less than 1 c/s. The corresponding relaxation times are clearly extremely long. In bulk specimens they will be even longer because of the greater thickness and are unlikely to be less than a second. However von Hippel and Alger/

Alger (1949) and Cooper et al. (1960) found it necessary to use pulses of duration as short as several microseconds in order to suppress the mechanism responsible for depressing the breakdown field above T_c. This suggests a relaxation time of the order of milliseconds at most. Unless an explanation for the discrepancy can be found it seems unlikely that the mechanism is the simple one originally suggested by von Hippel and Alger wherein positive ions migrate to the cathode and cause local field concentrations.

Before leaving the subject of space charge effects it should be noted that the dependence of breakdown field on temperature and on the duration t_{ap} of the applied voltage may be quite complicated. Fig.1.2 shows that von Hippel and Alger found a minimum breakdown field with voltages of intermediate duration (about 10^{-5} - 10^{-4} sec) when the temperature was below T_c. These authors describe their results on this subject as preliminary and their conclusion in itself would not have a high significance. Similar results have, however, been obtained by G.A. Vorob'ev (1956) for NaCl, KCl and KBr, but in KI the breakdown field remained constant as t_{ap} was decreased to about 10^{-8} sec and then increased steeply with further reduction in t_{ap}. The steep rise is probably due to a time lag to breakdown (Sub-section 1.3.3). Vorob'ev, like von Hippel and Alger, used sawtooth pulses of the shape sketched in Fig.3.1 (inset). The results of Konorova and Sorokina (1957) for KCl and KBr tend to indicate/

indicate a similar dependence, but it is not clear what pulse shape was used. Kuchin (1959) apparently using sawtooth pulses, observed a similar effect in NaCl, but found that with the changes in breakdown field there were associated variations in T_c, which first decreased and then returned to its d.c. value as t_{ap} was reduced to about 5×10^{-8} seconds. Kuchin's results are reproduced in Fig.1.3, where each point is stated to be the mean of 30 to 35 results. The results of Inuishi and Suita (1953) who found that breakdown fields measured with 1:100 μsec square pulses were lower than the d.c. values, are consistent with the hypothesis of a minimum breakdown field at pulse durations of this order.

The evidence for the reality of the effect is considerable. It may be associated with the existence of twomechanisms of space-charge formation having different relaxation times so that their effects cancel out at certain values of t_{ap}. However the results of different workers are conflicting on many details and it is not possible to come to a final conclusion.

1.3.2. Structure sensitivity of the breakdown field. It was pointed out in Section 1.1 that a disordered structure may affect the breakdown field. Evidence relating to this possibility is discussed in this sub-section.

Calderwood, Cooper and Wallace (1952, 1953) obtained histograms of the breakdown fields of potassium chloride crystals. Although extraneous mechanisms were excluded, the breakdown fields/

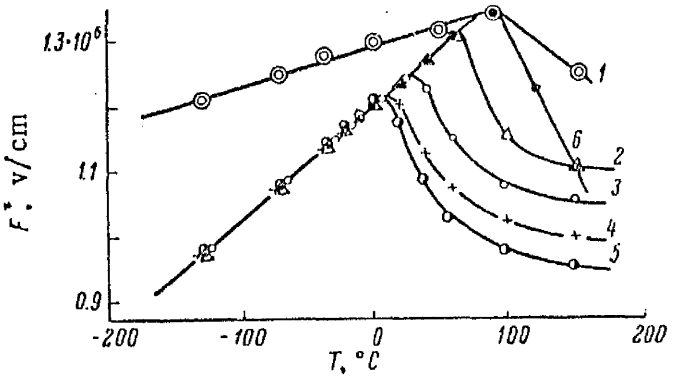


Fig.1.3

Breakdown field of rocksalt after Kuchin (1959). Single-shot pulses, apparently sawtooth. 1, 5 - 7 x 10^{-8} sec; 2, 10^{-7} sec; 3, 10^{-4} sec; 4, 10^{-5} sec; 5, 10^{-6} sec; 6, d.c.

fields of unannealed specimens ranged from about 0.5 to 1.5 MV/cm. In specimens carefully annealed before testing, on the other hand, the range was reduced to about 0.5 to 1.25 MV/cm and the mean value was lower. A similar but more pronounced effect was found in potassium bromide (Cooper 1962). These observations suggest that the effects of plastic strain in a crystal tend to increase its electric strength. Calderwood et al. confirmed this hypothesis by testing potassium chloride crystals that had been deliberately strained and showing that the mean breakdown field was increased and the range of values became wider. Inuishi and Suita (1955a) obtained further confirmation by showing that in potassium chloride specimens under mechanical stress applied with a weight the breakdown field increased with the load.

The most obvious interpretation is that increased electron scattering at dislocations and possibly at other crystallographic defects in the strained crystal leads to a rise in breakdown field. The observation of Inuishi and Suita (1955b) that the breakdown field decreased again if the specimen was aged (apparently still under load) for several minutes after the initial stressing may, as the authors suggest, be related to diffusion of defects to the surface of the specimen.

At fields of the order of the breakdown value, the mechanical stresses in an alkali halide crystal may be sufficient to induce plastic strain (Zavadovskaya 1951). This possibility was studied by Cooper and Wallace (1953, 1956) who found that the breakdown field

F_B/

F_B increased with the minimum field F_{st} necessary to produce strain as detected by the onset of light transmission through the crystal when positioned between crossed polariser and analyser. It is reasonable to take F_{st} as a measure of the concentration of dislocations in the crystal before it is strained by the field, because a high dislocation concentration will be associated with a high mechanical strength. This result therefore tends to confirm that crystals which contain large numbers of dislocations before the field is applied tend to have high electric strengths.

Most of the specimens tested broke down after the onset of plastic strain. Thus the number of dislocations at breakdown would exceed the number initially in the crystal. A.A. Vorob'ev (1956) has criticised the conclusions of Cooper and his colleagues on these grounds, stating that "the assertion that there is a difference in the measured electric strength of preliminarily deformed and undeformed samples has no meaning, since the samples broken down are already deformed". Vorob'ev's argument fails to explain the experimental fact that F_B increases with F_{st} and ignores the reduction in scatter and the lowering of the mean breakdown field observed by Calderwood et al. after annealing. On the other hand it is not obvious why F_B should be related to the initial rather than the final concentration of dislocations. Possibly breakdown has taken place in regions that were not strained by/

by the field. Cooper and Wallace (1953) gave photographs showing that light was transmitted only locally through the crystal after the onset of slip. This indicates that straining was also local.

Cooper and his colleagues have pointed out that wide scatter is to be expected in breakdown measurements even when extraneous effects have been excluded. Consequently it is essential to test large numbers of specimens. Many authors do not give details of this aspect of their work, and it is difficult to assess the significance of their results. Calderwood et al. also point out that whereas extraneous effects usually tend to reduce the breakdown field, plastic strain in a crystal tends to increase it. Now breakdown theories refer to ideal crystals. Hence if proper experimental precautions are taken the most significant values of breakdown field for comparison with theory will lie among the lowest measured, rather than among the highest as previously assumed.

It should be noted that although in the case of nearly perfect crystals studied by Cooper and his co-workers it has been established that disorder tends to increase the electric strength, other types of disorder tending to reduce it may occur in other solid forms.

1.3.3 Time lags. The steep rise in breakdown field observed by several workers when the duration of the applied voltage decreases to about 10^{-8} sec (Sub-section 1.3.1) may be due to the existence/

existence of a time lag to breakdown. When sawtooth pulses of the shape shown in Fig.3.1 are used, the applied voltage may overshoot the breakdown value so that the measured breakdown voltage rises (Cooper and Grossart 1956). With square pulses, the upper scatter limit of the experimental points will rise when the pulse duration is of the order of the total time lag t_d and so will the mean breakdown field. Kuchin (1959) has suggested that the breakdown field in these cases may exceed the critical field strength for mechanical disruption of the specimen, so that the latter will be the final mechanism of breakdown.

The values obtained by several workers for the mean statistical time lag τ_s and the formative time lag t_f are summarised in Table 1.1. The total time lags $t_d = t_f + t_s$ obtained by Vorob'ev and his colleagues are entered in the column headed "t_f" since these authors consider that t_s is negligible so that $t_d \simeq t_f$.

In the general case where both t_f and t_s are appreciable the relative frequency of total time lags greater than t will be (cf. Section 2.2)

$$\frac{n_t}{n_o} = e^{-\left(\frac{t - t_f}{\tau_s}\right)} \qquad (1.1)$$

Various workers have obtained results satisfying equation (1.1) and have thus been able to separate the statistical and formative time lags./

Table 1.1

Formative time lags t_f and mean statistical time lags τ_s as measured by various authors. Values are entered under τ_s or t_f according as authors claim to have measured statistical or formative time lags. "Stat." in the column headed "Method" indicates that the statistical and formative time lags were separated by a statistical method.

Author(s)	Crystal	Method	τ_s	t_f
Cooper and Grossart 1956	KCl,KBr	Stat.	1 - 2 μsec[1]	-
Cooper and Smith 1961	NaCl KCl	Stat. Partial b.d. channel	1 - 10 μsec[1,2]	- < 40 nsec
Cooper et al. 1960	KCl	Stat.	4 μsec approx.[1]	-
Kawamura et al. 1954	KCl KCl Mica	Stat.	240 nsec (7% o.v.) $\leq$ 60 nsec (20% o.v.) 10^{-8} - 10^{-4} sec, dependent on o.v.	- - $\leq$ 20 nsec
Inuishi and Suita 1952	KCl	Stat.	0.4 - 10 μsec decreasing with increasing applied voltage	0.5 - 1 μsec decreasing with increasing applied voltage

1. Below critical temperature. Above T_c values were distributed about a mean.
2. Dependent on cathode material.

Contd./

Table 1.1 (contd.)

Author(s)	Crystal	Method	τ_s	t_f
Vorob'ev and Vorob'ev 1958a	NaCl	Direct observation of single sawtooth pulse (time from start of pulse to b.d. measured)	-	4 - 17 nsec (L = 0.15 mm)
	NaCl		-	10 - 30 nsec (L = 0.3 mm)
	KCl		-	3 - 16 nsec
	KBr		-	2 - 22 nsec
	KI		-	2 - 21 nsec
Mel'nikov 1959	NaCl	Direct observation of single flat-topped pulse	< 1 nsec	2 - 3 nsec
	KCl		< 1 nsec	2 - 3 n sec
Sonchik 1958a	NaCl	Direct observation of single flat-topped pulse	-	40 - 50 nsec (15% o.v.)
	NaCl		-	30 - 40 nsec (25% o.v.)

lags. These authors' results are marked "stat." in Table 1.1. This method of finding τ_s has been criticised by G.A. Vorob'ev (1962) as failing to establish that the calculated statistical time lag has a physical existence. It is difficult to agree with Vorob'ev when the observed distribution of time lags is the same as the theoretically predicted one. Even if t_f showed statistical variation as a result of thermal fluctuations or of experimental errors one would expect values distributed about a mean rather than the distribution of equation 1.1.

Vorob'ev and his co-workers themselves determined total time lags of the order of tens of nanoseconds at most, and whether their assumption that the time lags are purely formative is correct or not the statistical time lag cannot be greater than the total time lag. Cooper and his colleagues, on the other hand, obtained time lags of the order of microseconds. Possibly Vorob'ev and his associates have obtained small values because of the high over-voltages used. Sonchik (1958a and b) measured t_d at fields 15% and 25% greater than the field strength for a 90% breakdown probability. The actual percent overvoltages for individual specimens would on the average be even greater. Cooper and his colleagues determined breakdown fields by applying successive pulses of amplitudes increasing by a constant fraction, in some cases as small as 1%, and measured the statistical time lags in the course of this procedure. The overvoltages with respect to the breakdown voltages/

voltages of each individual specimen would therefore be very small and the statistical time lag correspondingly large.

The intermediate values of time lag measured by Kawamura et al. (1954) may be similarly explained since these workers used fixed overvoltages of 7% and 19% with respect to the mean breakdown field.

Thus the time lags measured by Vorob'ev and his associates may well be almost purely formative as the authors suggest. The fact that Cooper and Smith (1961) estimated the formative time lag from the duration of the applied voltage and the length of a partial breakdown channel as being of the same order tends to support this view. On the other hand there is little direct evidence that the statistical time lag is negligible at high overvoltages. Vorob'ev and Vorob'ev (1958a) found the breakdown fields of uncoloured rocksalt crystals and of coloured crystals under illumination to be the same when measured with pulses of duration 20 - 30 nsec. These authors state that as a result of voltage overshoot one would expect a reduced breakdown field in the coloured crystals if there were an appreciable statistical time lag, presumably since the electron supply is greater in the coloured crystals and τ_s correspondingly shorter (see also Mel'nikov 1959). However Cooper and Smith obtained evidence that the electrons initiating breakdown originate from the cathode, and depressed breakdown fields in coloured crystals are usually ascribed to space-charge/

charge effects. Secondly, although Vorob'ev et al. (1960) stated that discharge channel formation began as soon as the breakdown voltage was applied, it is not clear how accurately this observation could be made. Finally, Sonchik (1958a) found that t_d increased with temperature in rocksalt crystals and explained this observation on the assumption $t_d \simeq t_f$ with t_s negligible by suggesting that the stronger lattice vibrations at higher temperatures reduce the velocity with which an avalanche is propagated. However if breakdown occurs by an avalanche mechanism his result is also consistent with assuming $t_d \simeq t_s$ with t_f negligible, because in view of the increased electron scattering at higher temperatures one will on the average have to wait longer for an electron to be accelerated to the ionisation potential.

Further work is necessary to clarify this question, but the tendency of the available evidence is to suggest a statistical time lag of several microseconds at sufficiently low overvoltages. This is consistent with avalanche breakdown theory but not with the simple theories of collective and field-emission breakdown. However Cooper and Smith (1961) have pointed out that a statistical time lag may conceivably exist even in collective breakdown since the electron density may reach its necessary high value for this mechanism only during random fluctuations. The existence of a statistical time lag cannot therefore be taken as conclusive evidence/

evidence for an avalanche mechanism.

In passing it may be noted that Cooper and Smith found different statistical time lags in sodium chloride with cathode surfaces of different metals. This suggests that the cathode, if of metal, is the normal source of the electrons initiating the breakdown process. According to Cooper and Smith the nature of the cathode surface does not affect the breakdown field. Von Hippel and Alger (1949), on the other hand, found a lower breakdown field in potassium bromide crystals when the cathode was of metal than when it was of potassium bromide solution. However this contradiction does not alter the conclusion as to the origin of the breakdown electrons.

1.3.4 Pre-breakdown noise. A noisy pre-breakdown current is an expected characteristic of an avalanche mechanism and certain authors who have observed pre-breakdown noise have regarded it as evidence for this type of mechanism (Haworth and Bozorth 1934, Yamanaka and Suita 1952, Kawamura and Onuki 1952). It was not verified that the observed noise was actually due to avalanches. Powers and Suita (1955) showed that the frequency spectrum of the pre-breakdown noise in mica and KCl contained no large component of frequency greater than about 10^4 c/s, whereas if the noise resulted from pre-breakdown avalanches one would expect a prominent component with a frequency of the order of the reciprocal of the statistical time lag, i.e. about 10^6 c/s according to the results of/

of Cooper and his associates. The fact that the observed frequencies were lower could be accounted for if the statistical time lag were unusually long, as is possible since Powers and Suita worked at field strengths in the pre-breakdown region. However in this case one would expect a stronger dependence of noise current on field strength than was actually observed. The authors themselves suggested activation and decay of sensitive spots on the cathode as a tentative explanation of the noise.

The absence or near-absence of pre-breakdown noise in the frequency region corresponding to the statistical time lag is unfavourable to the suggestion of an avalanche breakdown mechanism. However if the avalanche size increased very rapidly with field strength as suggested by the calculation in Section 2.2, the noise current might be appreciable only at field strengths within a narrow interval below the breakdown value, and would be difficult to detect.

1.3.5. Effect of specimen thickness The variation of breakdown field with thickness may give information on the breakdown mechanism and has been studied by several workers. Ryu and Kawamura (1954) were unable to detect any variation in potassium chloride in the thickness range 10^{-2} to 10^{-1} mm. However unless adequate precautions are taken to avoid structure effects it is unlikely that a variation as small as that expected in this thickness range./

range could be observed. Cooper and Smith (1961) obtained a high negative correlation coefficient between the minimum values of electric strength of sodium chloride crystals and their thicknesses in the range 0.1 to 0.6 mm., while Kostrygin (1960) found that the electric strength of the same substance increased from about 2.6 to about 7.5 MV/cm as the thickness was decreased from about 160 000 Å to 32 000 Å. This evidence suggests that a dependence does exist.

Although the thickness dependence has not been widely studied in single-crystal alkali halides, several workers have investigated other thin systems, and some of them have attempted to compare the observed variations with those predicted by theories. According to equation 2.4 (the Seitz-Stratton equation - Section 2.2), a graph of $\frac{1}{F_B}$ versus log $\frac{L}{F_B}$ will be a straight line. Kawamura and Azuma (1953) plotted in this way their results for alumina films formed by anodising evaporated aluminium films, and obtained straight lines at 198°K, 300°K, and 373°K. Using equation 2.4 they then determined values for the electron mobilities at these temperatures. The results of Lomer (1950) for similarly prepared alumina films, however, are in closer accordance with the relation

$$F_B = \text{const.} L^{-\alpha} \qquad (1.2)$$

with $\alpha = 0.28$, than with the Seitz-Stratton relation. This can be seen by comparing Lomer's results as a graph of log F_B versus log L (Fig.1.4) with the same results as a graph of $\frac{1}{F_B}$ versus log $\frac{L}{F_B}$ (Fig.1.5)/

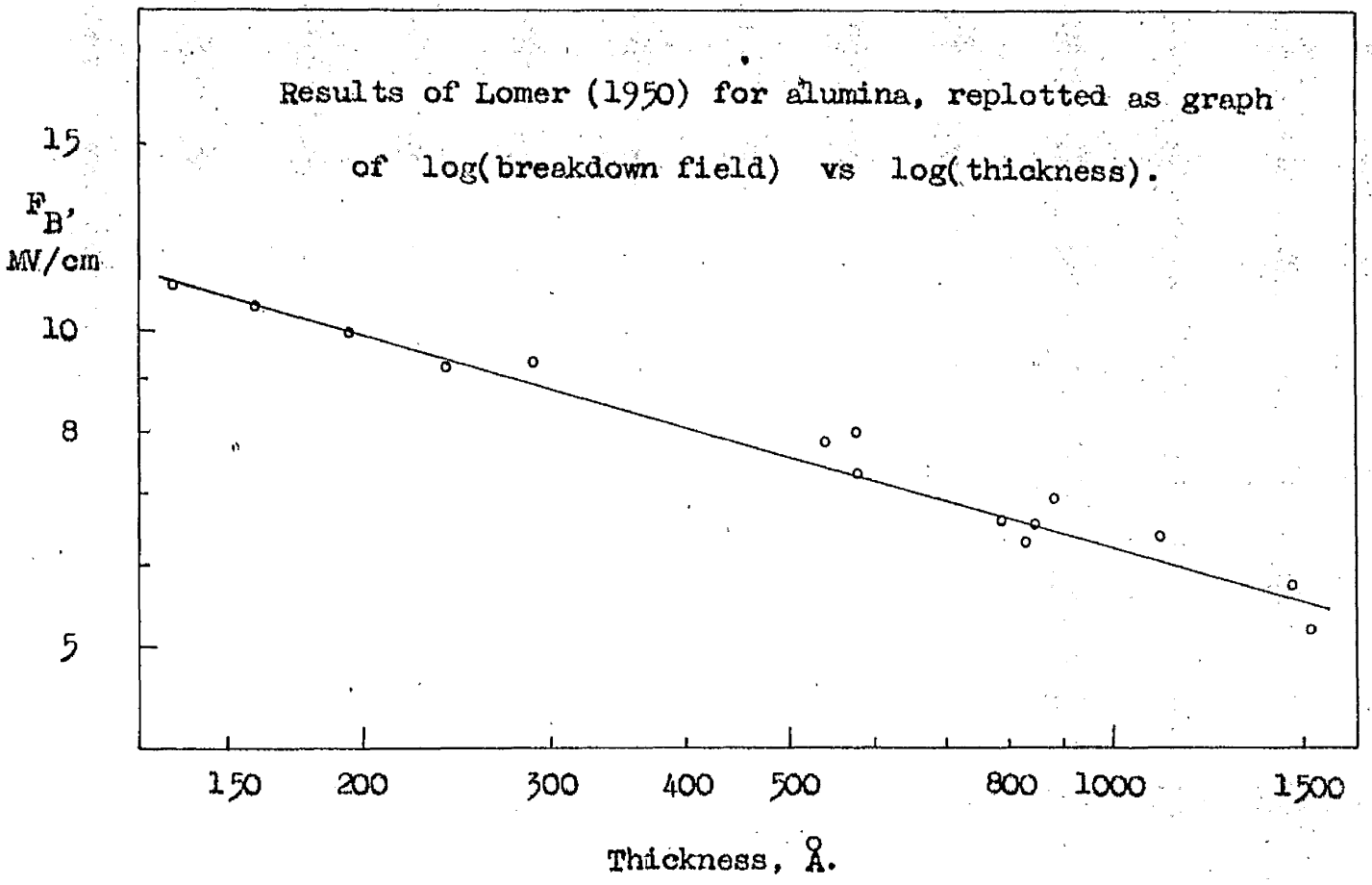

Results of Lomer (1950) for alumina, replotted as graph of log(breakdown field) vs log(thickness).
15
F_B, MV/cm
10
8
5
150
200
300
400
500
800
1000
1500
Thickness, Å.

Fig.1.4

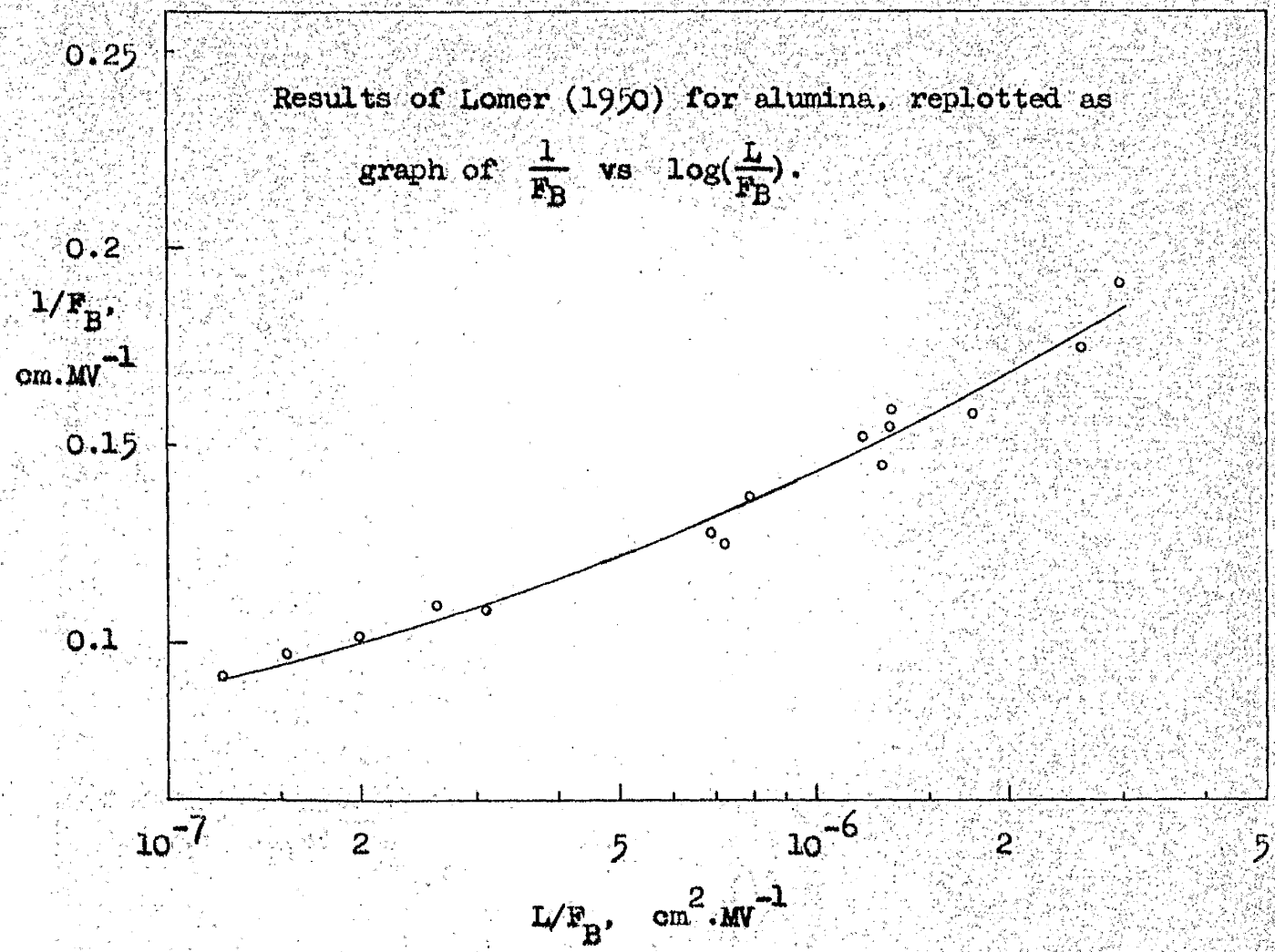

Results of Lomer (1950) for alumina, replotted as graph of $\frac{1}{F_B}$ vs $\log(\frac{L}{F_B})$.
0.25
0.2
0.15
0.1
$1/F_B$, cm.MV^{-1}
10^{-7}
2
5
10^{-6}
2
5
L/F_B, cm^2.MV^{-1}

Fig.1.5

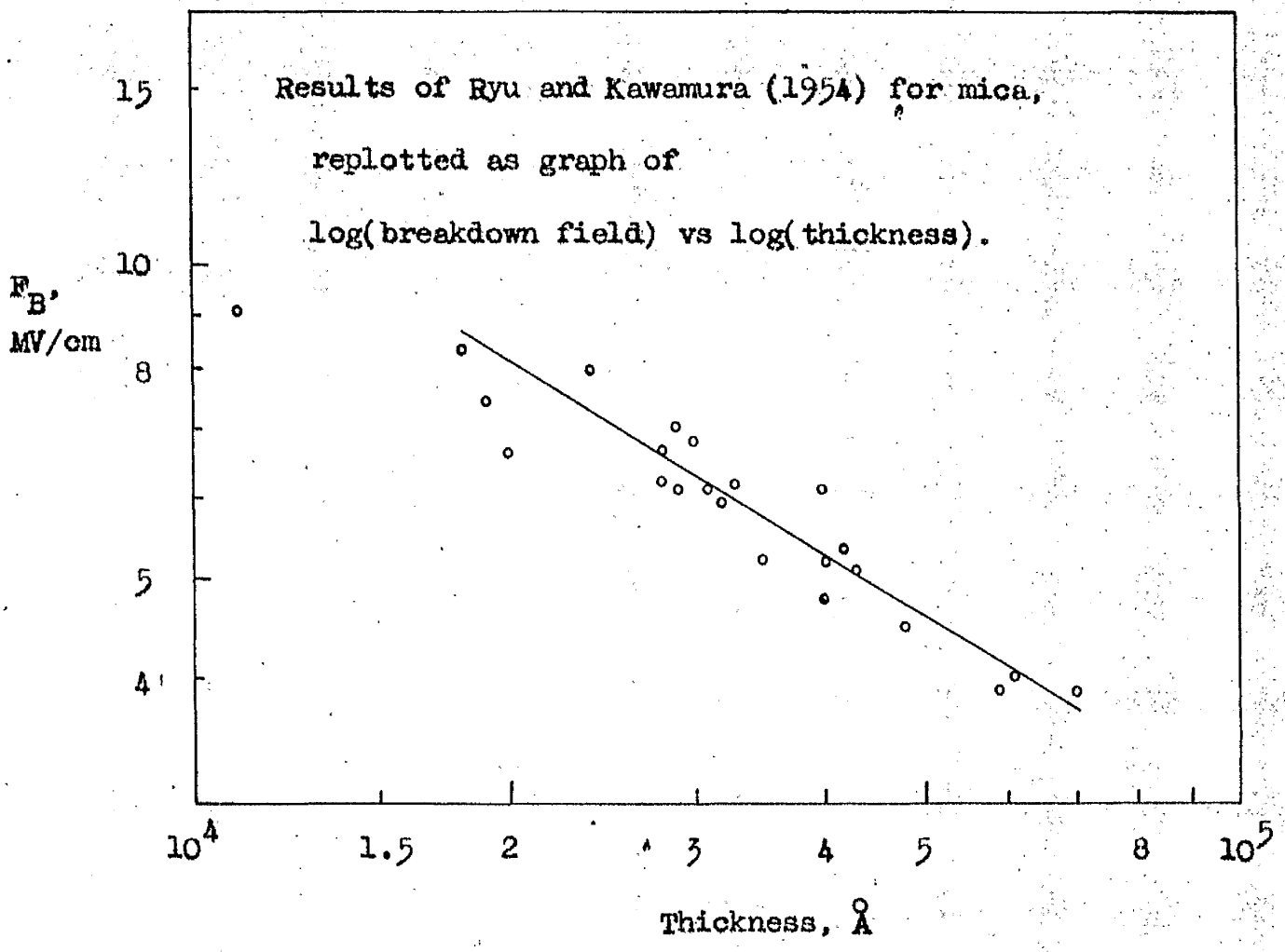

Results of Ryu and Kawamura (1954) for mica,
replotted as graph of
log(breakdown field) vs log(thickness).
15
10
8
5
4
F_B, MV/cm
10^4
1.5
2
3
4
5
8
10^5
Thickness, Å

Fig.1.6

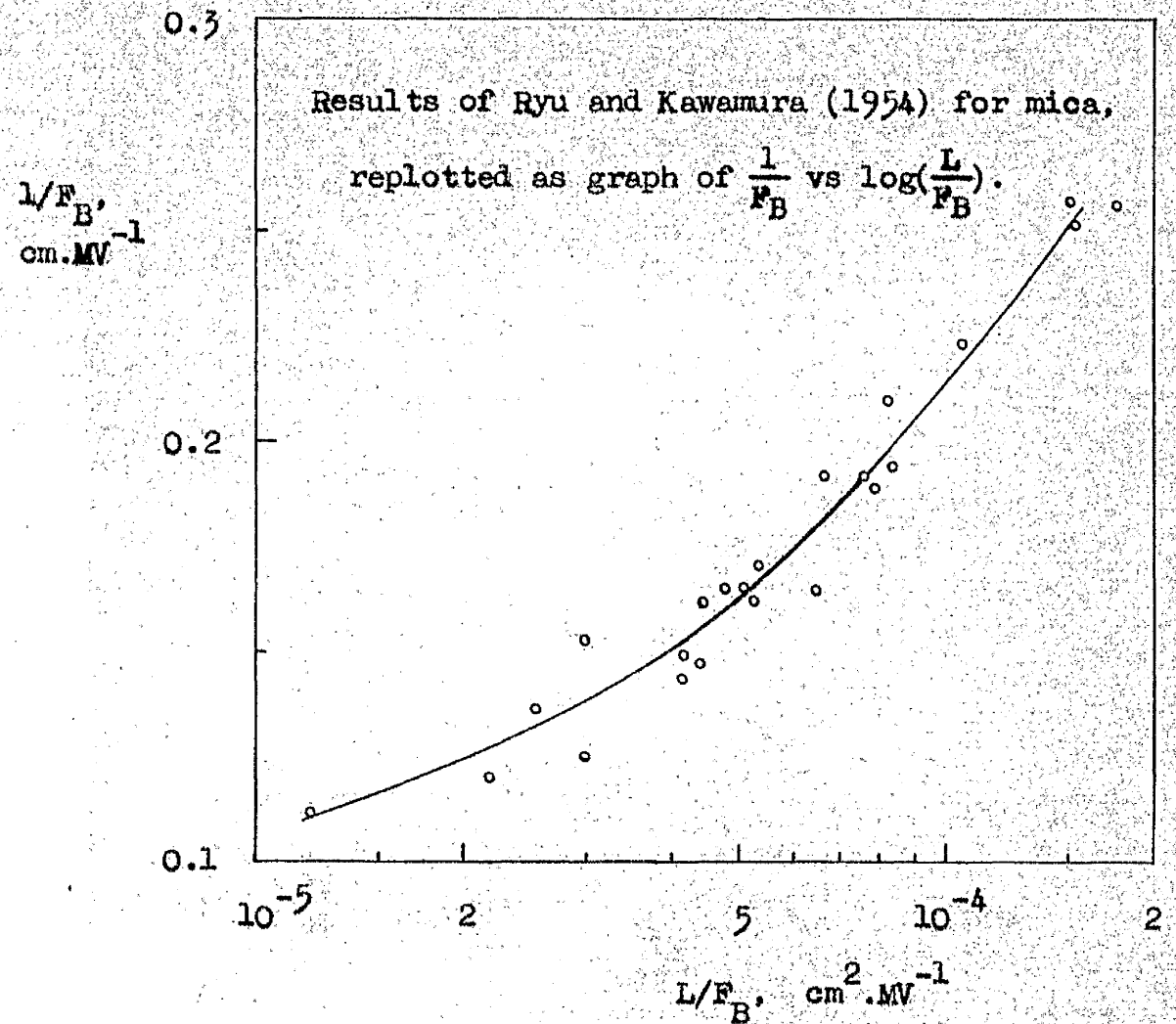

Results of Ryu and Kawamura (1954) for mica,
replotted as graph of $\frac{1}{F_B}$ vs $\log(\frac{L}{F_B})$.
$1/F_B$, cm.MV^{-1}
0.3
0.2
0.1
10^{-5}
2
5
10^{-4}
2
L/F_B, cm^2.MV^{-1}

Fig.1.7

(Fig.1.5). A relation of the form (1.2) was predicted by Forlani and Minnaja (1964) on theoretical grounds with α between 0.25 and 0.5 (Section 2.2). These authors themselves state that equation 1.2 was satisfied with $\alpha = 0.5$ in the results of Morrill and West (1963) for alumina. The results of Kawamura and Azuma are thus unusual in satisfying the Seitz-Stratton relation. Unfortunately their graphs do not permit recalculation back to the values of L and F_B with sufficient accuracy for a plot of log F_B against log L to be useful.

In mica, the results of Austen and Whitehead (1940) cannot be satisfactorily fitted to either equation although they do indicate an increase with decreasing thickness. A dependence was also found in this material by Ryu and Kawamura (1954). Kawamura again fitted results to the Seitz-Stratton equation and calculated electron mobilities, but by plotting the results as graphs of log F_B versus log L and of $\frac{1}{F_B}$ versus log $\frac{L}{F_B}$ it is easy to show that equation 1.2 with $\alpha = 0.64$ is a better empirical description of the results. The graphs are shown in Figs. 1.6 and 1.7.

In evaporated films, the results obtained by Plessner (1948) in general indicate a thickness dependence. Plessner's work is reviewed in Section 1.1.

It seems to be established that a decrease with increasing thickness exists in the substances studied by previous workers. This is strong evidence for avalanche breakdown. Until however

more/

more results are available it is unwise to draw conclusions regarding the form of the dependence and hence regarding the exact type of avalanche mechanism.

1.4 Aims of the Present Work.

Evidence has just been presented that in various solid forms the breakdown field decreases with increasing specimen thickness. Flessner's investigation appears however to be the only attempt to detect a similar variation with thickness in evaporated films. It is therefore desirable that Flessner's observation should be confirmed. This the present author has attempted to do.

Dependences of this kind are of particular interest in thin specimens since avalanche breakdown theories predict that any dependence of breakdown field on thickness will be strong at small thicknesses. This suggests that vacuum-deposited layers may be very useful in studying the breakdown mechanism, for they can readily be produced at small thicknesses. On the other hand the film structure may affect not only the magnitude of the breakdown field but also its thickness dependence. It will be important to bear this in mind in interpreting the results, particularly if the observed breakdown fields differ from the bulk values.

The present work was first suggested by Weaver's preliminary observation (Section 1.1) that the breakdown fields of evaporated dielectric films were surprisingly low and seemed to be affected by moisture. The present author has attempted to extend these observations/

observations and to relate thin-film and bulk breakdown by comparing the results of measurements on evaporated layers with published results for bulk materials. It was necessary to verify that the low breakdown fields were not due to extraneous causes. The experimental precautions taken to avoid non-intrinsic mechanisms and electrode effects are described in Chapter 3 and further discussed in Sections 6.1 to 6.3. More fundamental explanations of the low values of breakdown field in terms of the film structure could then be sought.

It is necessary to use evaporated metal electrodes in order to reproduce Weaver's experimental conditions as nearly as possible. This electrode system has the further advantage over a sphere-end-plane configuration of approximating more closely to the design that might be found in an evaporated capacitor, and of avoiding the danger of contamination of the spherical electrode by films of oxide and of diffusion pump oil. On the other hand edge effects may occur with evaporated electrodes. The precautions taken to reduce this risk are discussed in Sub-section 3.1.1 and Section 6.6.

The principal objectives of the present work may now be summarised:

1. To extend the observations made by Weaver on the breakdown of dielectric films sandwiched between evaporated metal electrodes, and to relate thin-film and bulk breakdown by comparing the results with those obtained by previous workers on bulk materials.

2/

2. To obtain information on the breakdown mechanism.

3. To study the effects of moisture on the breakdown of the layers.

1.5 Choice of Dielectrics.

To compare results of breakdown measurements on evaporated films with published results for bulk materials, it is desirable to choose a material whose electric strength can be reasonably simply calculated from existing theories and whose breakdown has been widely studied experimentally. Both conditions are well satisfied by the commoner alkali halides. Unfortunately most alkali halides are readily soluble in water and are therefore not only unpromising as capacitor dielectrics but also likely to be unsuitable for adsorption studies. Lithium fluoride is relatively insoluble, but its electric breakdown in bulk form has received only limited attention (Section 1.6). Moreover although the properties of lithium fluoride films are fairly well known, the soluble alkali halides in thin film form have been largely neglected, perhaps partly because of their lack of immediate practical usefulness and partly because they undergo extensive structural changes on exposure to atmospheric moisture (Weaver 1962, Mullen 1964) and are therefore difficult to study.

As a compromise the author investigated lithium fluoride and sodium chloride. The latter substance has been the subject of extensive breakdown studies in bulk form. Results have also been obtained for cryolite (Na_3AlF_6). This material has been widely/

widely used for optical purposes because of its ease of evaporation, low solubility, and good stability in thin film form. It is therefore potentially useful as a capacitor dielectric. Results of investigation of its electrical properties, including electrical breakdown fields, may therefore have practical importance in the development of thin film capacitors. Since the experiments described here were performed, the results obtained by Macfarlane (1964) have shown that cryolite has promising dielectric properties for applications in evaporated capacitors.

1.6 Note on the Electric Strength of Ideal Crystals of Lithium Fluoride.

Von Hippel (1935) measured the electric strengths of several alkali halides (cf. Whitehead 1951, p.61). The values quoted for lithium fluoride and sodium chloride were respectively 3.0 MV/cm and 1.5 MV/cm. If one accepts the conclusion of Calderwood, Cooper and Wallace (1953) that the lowest experimental results not affected by extraneous processes are the most nearly equal to the breakdown field of an ideal crystal, one will regard von Hippel's results as high. The minimum breakdown field obtained by Cooper and Smith (1961) for sodium chloride was about 0.75 MV/cm. On this basis one may estimate the minimum value in lithium fluoride at very roughly 1.5 MV/cm.

CHAPTER 2

THEORIES OF INTRINSIC BREAKDOWN

The physical models on which the various breakdown theories are based were briefly described in Section 1.1. In the present chapter the theories are discussed in greater detail.

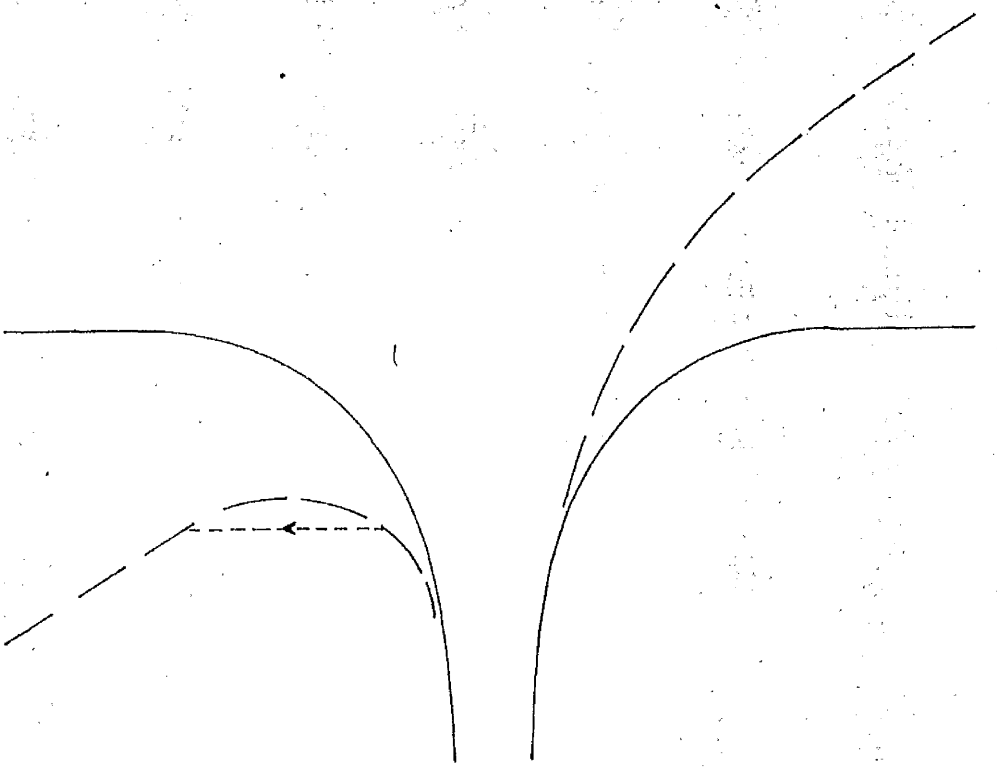
2.1 Field Emission Breakdown.

This theory is based on a paper by Zener (1934). The bound electrons in a dielectric are situated in potential wells in the neighbourhood of the lattice ions or atoms (Fig.2.1, continuous line). If a strong field is applied the potential diagram becomes distorted (broken line) and the electron may escape from the potential well by tunnelling as suggested in the diagram. For the number $\frac{dn}{dt}$ of electrons escaping in this way per second under an applied field F, Zener obtained the equation

$$\frac{dn}{dt} = \frac{eFa}{h} \cdot \exp\left(-\frac{\pi^2 m a E_g^2}{h^2 |eF|}\right), \qquad (2.1)$$

where a is the lattice constant of a one-dimensional lattice and E_g the energy gap between the filled band and the valence band. $\frac{dn}{dt}$ varies with F in the manner sketched in Fig.2.2.

This suggestion was criticised on the grounds that to account for the catastrophic nature of breakdown $\frac{dn}{dt}$ should increase almost discontinuously at some value of field strength. In the light of later developments in breakdown theory this criticism no longer seems justified. As Seitz (1949) implies, the fact that free electrons are being emitted does not necessarily ensure that breakdown will follow; one must in effect calculate the current density due/



Zener effect. Potential well in absence of field (continuous line) and in presence of field (broken line). Dotted line with arrow indicates electron tunnelling.

Fig.2.1

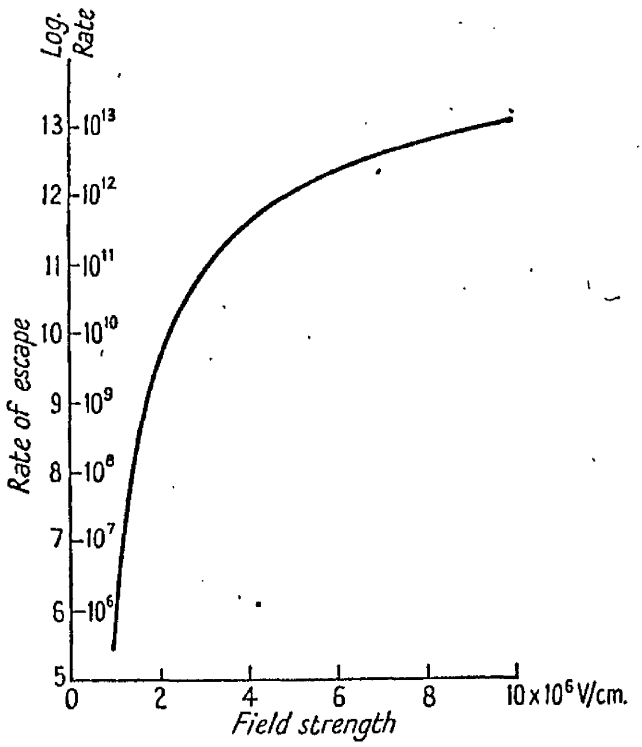
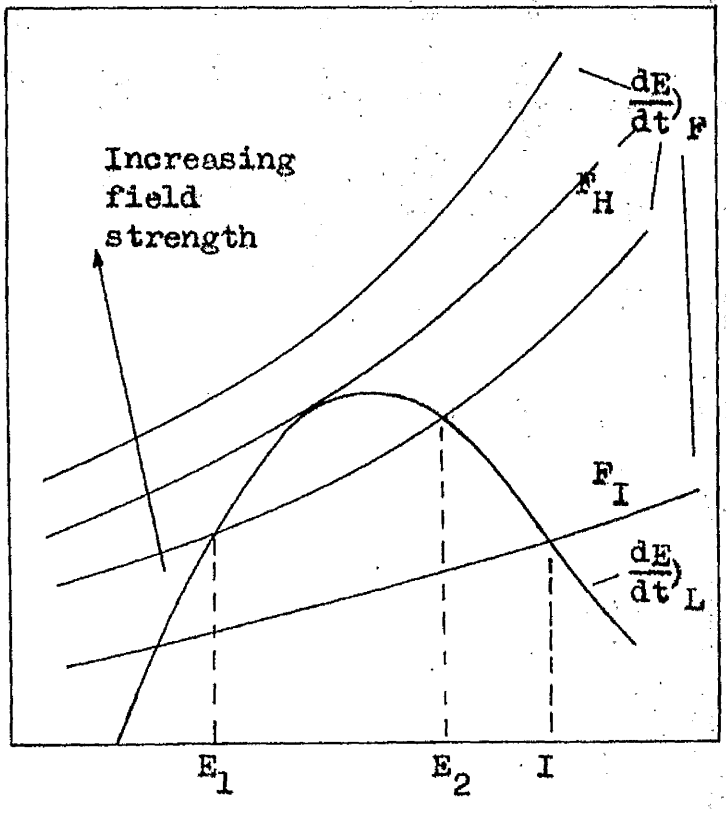


Fig. 2.2

Number of electrons emitted from potential wells per second as function of applied field, according to Zener (1934). (After Whitehead 1951).



Variation with electron energy of rates of gain and loss of energy.

(After Stratton 1961.)

Fig.2.3

due to these free electrons and compare it with a critical current density j_B for breakdown. Thus in Fig.2.2 to every value of rate of electron escape there will correspond a certain value of current density. The value of field strength at which this current density exceeds j_B will be the breakdown field F_Z (say) and will be a critical value.

The theory has been extended along these lines by Franz (1956), and also by Stratton (1961), who points out that F_Z will usually be higher than the breakdown fields for other mechanisms in insulators. Thus an insulator will usually have broken down by another mechanism before field emission breakdown can take place. There is, however, some evidence for field emission breakdown in semiconductors under certain conditions (Chynoweth and McKay 1957, Williams 1962, Boer et al. 1962).

2.2 Breakdown by Impact Ionisation: Electron Avalanches.

The suggestion that breakdown of solid dielectrics results from disruption of the structure by avalanches of electrons freed by impact ionisation was first made by Guntherschultze (1923) and later developed by von Hippel (1932, 1934, 1935, 1937).

A free electron in a dielectric will lose energy to the lattice vibrations at a rate $(\frac{dE}{dt})_L$ dependent on the energy E of the electron and the lattice temperature T. In Fig.2.3 (after Stratton 1961) the variation of $(\frac{dE}{dt})_L$ with E is sketched. Von Hippel argued that since the majority of the free electrons will have energies

below/

below the value corresponding to the maximum in the curve, the lattice vibrations will in effect constitute a 'friction barrier' against acceleration of electrons to higher energies unless the applied field is high enough to supply energy to these low energy electrons at a rate greater than $(\frac{dE}{dt})_L$.

The variation with E of the rate $(\frac{dE}{dt})_F$ at which electrons gain energy from the field is also sketched at several field strengths in Fig.2.3. If all the low energy electrons are to be accelerated, the field strength must have the value F_H, or nearly this value, at which the curve for $(\frac{dE}{dt})_F$ is tangential to that for $(\frac{dE}{dt})_L$. For this reason F_H is usually taken as the breakdown field according to von Hippel's 'low-energy' criterion, although von Hippel pointed out that according to his ideas breakdown could take place at a slightly lower field (von Hippel and Alger 1949).

Fig.2.3 illustrates that F_H is the field strength above which no solution exists to the energy balance equation $(\frac{dE}{dt})_L = (\frac{dE}{dt})_F$. It therefore seems reasonable to take F_H as the breakdown field. However at field strengths below F_H the higher of the two solutions, E_2 (Fig.2.3), corresponds to an unstable equilibrium and electrons of energy greater than E_2 will increase their energy indefinitely unless there exists another mechanism of energy loss, alternative to collisions with the lattice vibrations (Frohlich 1947b). Thus a steady state is impossible even at low field strengths. Frohlich (1937, 1939) assumed that the alternative mechanism would be/

be impact ionisation of the lattice ions and on this basis proposed a different breakdown criterion from von Hippel's. Referring to Fig.2.3, E_2 will be greater at low field strengths than the ionisation potential I of the ions. All electrons of energies in excess of E_2 will therefore be able to dissipate their energy by ionising collisions, which in this region of field strengths provide a means whereby the dielectric retains its stability rather than a breakdown mechanism. At higher field strengths, however, where E_2 is less than I as shown in the diagram, electrons in the range E_2 to I will only be able to increase their energy and instability will result. Frohlich assumed that this would lead to breakdown, and therefore proposed as the critical breakdown field F_I, the value of F at which $E_2 = I$.

Von Hippel and his colleagues replied to Frohlich's criticism by expressing the view that the number of electrons increasing their energy according to Frohlich's ideas would be so small that insufficient energy would be given to the lattice to disrupt it (von Hippel and Alger 1949). However in von Hippel's theory all the free electrons would have to be accelerated to produce breakdown, and this assumption of the number of electrons required is itself quite arbitrary. In neither of these early theories was there an attempt to calculate a critical current density for breakdown.

The expression obtained by Frohlich for the breakdown field is/

is

$$F_I = 1.64 \times 10^5 \left(\frac{\rho}{G}\right)^{1/3} \cdot \lambda_o \frac{\varepsilon_s - \varepsilon_\infty}{\lambda_1^{3/2}} \left\{1 + \frac{2}{e^{h\nu_1/kT} - 1}\right\}^{1/2}, \quad (2.2)$$

where ρ is the density of the dielectric, G is its molecular weight, λ_o is the wavelength of the first ultra-violet absorption maximum in Å, λ_1 is the reststrahlen wavelength in microns, ν_1 is the reststrahlen frequency, and ε_s and ε_∞ are the static and optical dielectric constants. Frohlich used a quantum-mechanical perturbation method in calculating the electron-lattice interaction. The validity of this procedure has been discussed by Seitz (1948, 1949) who concludes that at collision frequencies of the order that occur at field strengths near the breakdown value methods of this type are to be regarded as "semi-quantitative". Nevertheless three of Frohlich's predictions are important. Firstly, the breakdown field will increase with temperature. Secondly, if an avalanche theory applies, the breakdown field will rise when the thickness of the specimen decreases to approach the mean free path of an electron in the material, since the electrons then have a shorter distance in which to reach the ionisation potential and must be accelerated faster. This has obvious relevance to the breakdown of thin specimens. Thirdly, Frohlich pointed out that a dielectric cannot break down by a mechanism of this kind at an applied voltage less than the ionisation potential expressed in electron volts.

Callen/

Callen (1949) using the method of Frohlich (1937) calculated the value of breakdown field at 0°C according to von Hippel's criterion. The final equation is

$$(F_H)_0 = 134 \times 10^6 (\hbar\omega)_{eV} \cdot \frac{\varepsilon_s - \varepsilon_\infty}{(\varepsilon_s \varepsilon_\infty^3)^{1/2}} \cdot \frac{m^*}{m} \quad V/cm, \qquad (2.3)$$

where $(\hbar\omega)_{eV}$ is the reststrahlen energy in eV. The only disposable constant in this equation is the ratio $\frac{m^*}{m}$, which will be of order 1. Callen also gave a method of calculating F_H at other temperatures and predicted that F_H would increase slowly with temperature. (It is sometimes stated that in von Hippel's theory electrons are accelerated along the field and the energy gain is proportional to the field strength, whereas in Frohlich's theory the electrons change direction when they collide and the energy gain is proportional to the square of the field strength. Callen follows Frohlich on this point although using von Hippel's criterion for the breakdown field.)

The first attempt to approach the problem in terms of a critical current density for breakdown was made by Seitz (1949). It was assumed that breakdown was caused by localised avalanches initiated by single electrons. Actual values of current density were not considered, but instead the critical avalanche size (number of electrons) for breakdown was estimated. Breakdown was assumed to occur if each ion or atom in the path of the avalanche received at least 10 eV of energy. Seitz estimated the density of free/

free electrons of energy near the ionisation potential that would be necessary to transfer this amount of energy, and hence, using a value for the volume of the discharge channel estimated by assuming an effective diffusion coefficient of 1 cm^2/sec for transverse diffusion of electrons in the avalanche, obtained a rough value of 10^{12} for the critical avalanche size for breakdown. Since $2^i = 10^{12}$ when $i = 40$, it follows that if two electrons are free for further ionisation after each ionising collision, the number of such collisions made by the starting electron in an avalanche of the critical size for breakdown will be about 40.

Using Seitz's approach, Stratton obtained an equation for the breakdown field. Provided the relaxation time of the conduction electrons can be assumed equal to the mean time between collisions, the relation may be written

$$F_A = \frac{H}{\ln\left(\frac{e}{m} \cdot \frac{L}{F_A[\mu(E_1)]^2 i}\right)}, \qquad (2.4)$$

where H is a constant field and $\mu(E_1)$ is the electron mobility corresponding to the mean energy of stable free electrons at the breakdown field, which is approximately the energy at the lower (stable) solution of the energy balance equation (Fig.2.3). The breakdown field decreases with increase in the specimen thickness L, and the variation is appreciable at thicknesses of the order of hundredths of a millimetre. This is in contrast to the earlier suggestion by Frohlich that a dependence of this kind would be noticeable only at thicknesses approaching the mean free path of an/

an electron. However Stratton also points out that breakdown by Seitz's mechanism is theoretically impossible below a critical thickness

$$L' = \frac{H \exp(1)}{\zeta}, \qquad (2.5)$$

where

$$\zeta = \frac{e F_H^2}{k \Theta} \cdot \frac{2 (1 + e^{\Theta/T})^{-1} + 1}{i}, \qquad (2.6)$$

Θ being the Debye temperature of the lattice, T the lattice temperature, and H and i having the same significance as in equation 2.4. Stratton expresses the view that in practice a large increase in breakdown field would be observed at thicknesses decreasing towards L'. Now in sodium chloride $F_H \simeq 1.4$ MV/cm and $\Theta \simeq 300^{\circ}$K. This gives $\zeta \sim 10^{13}$ V/cm^2 at room temperature (taking i as about 40; its precise value does not affect the order of magnitude). If $H = 3.8 F_H$ (Seitz's estimate) we then find $L' \sim 100$ Å. Thus when the thickness x decreases to several hundred Å a further increase with decreasing thickness may be superposed on the variation predicted by equation 2.4.

In Seitz's breakdown mechanism it is reasonable to expect electron avalanches below the critical size at field strengths somewhat less than the breakdown value. These will not lead to breakdown but will lead to a noisy pre-breakdown current. However Kawamura et al. (1954) have pointed out that such avalanches would be surrounded by intense radial fields which might greatly exceed the breakdown value. To estimate the radial field we may assume that/

that it would be approximately spherical since the electrons would be concentrated in the advancing tip of the avalanche. Then taking the radius of the avalanche tip to be 10^{-3} cm, on Seitz estimates, and assuming a dielectric constant of 10, we may estimate the radial field at the surface of the avalanche channel as approximately $10^{-3}n$ MV/cm, where n is the avalanche size. This value will if anything be too low, because the total time required for the avalanche to form will not exceed about 10^{-6} seconds and the dielectric constant will be smaller than 10 at the frequencies concerned. Thus with a breakdown field of about 1 MV/cm, the radial field would exceed the breakdown value if an avalanche reached a size of 10^8 electrons near the anode. Although breakdown would not necessarily ensue, these considerations suggest that the critical avalanche size should be taken as about 10^8 rather than 10^{12} electrons, corresponding to about 25 instead of 40 ionising collisions of the starting electron. However this objection to Seitz's physical model may not be a serious one, because Seitz himself pointed out that the avalanche size would increase very rapidly with field strength. The breakdown field is therefore not very sensitive to the critical avalanche size.

This point may be clarified by a simple calculation. In equation 2.4, the effect of the factor 1 will not be noticeable if $\frac{e}{m} \cdot \frac{L}{F_A/\mu^2} \gg \frac{1}{i}$. F_A is typically about 1 MV/cm.

Electron mobilities in some alkali halides at low field strengths have been calculated by Hofstadter (1949) from the theory of Frohlich and Mott (1939). The theoretical values at 300°K range from about 7 $cm^2/Vsec$ for potassium bromide to 216 $cm^2/Vsec$ for lithium fluoride. At higher field strengths the mobility will alter as a result of the greater mean electron energy (Fig.2.3), and according to Frohlich (1937) the change will be an increase. However the curve for $(\frac{d\bar{u}}{dt})_L$ rises steeply from the energy axis (cf. Callen 1949). Consequently the mean electron energy will not greatly exceed its zero-field value and the change in mobility will be small. In practice the mobilities are actually likely to be less than the values quoted above because of electron trapping (Collings and Hirsch 1964). Even if the theoretical value for lithium fluoride is assumed, however, $\frac{e}{m} \cdot \frac{L}{F_A \mu^2}$ is as large as about 0.38 even in a specimen of thickness as small as 1000 Å, whereas $\frac{1}{i}$ is of the order of $\frac{1}{25}$. Thus the avalanche size is unlikely to be important in alkali halides at room temperature except in very thin specimens of substances with a high electron mobility. In passing, it may be noted that if i is taken as 1 as in Frohlich's early theory the predicted breakdown field may not be very different.

Cooper and Fernandez (1958) have drawn attention to what may be a more serious difficulty. In the presence of a radial field an electron avalanche would not be propagated along the applied field but would wander at random through the specimen. Discharge paths/

paths through solids have been observed by numerous authors to be straight cylindrical channels in the early stages of their formation (e.g. von Hippel 1931 a and b, Davisson 1959, Cooper and Fernandes 1958).

These difficulties may be avoided by regarding the avalanche process as a multiplication of electron density throughout the area exposed to the field rather than considering localised avalanche initiated by single electrons. (Dallos 1951, Franz 1952, Vaulton 1955). Both avalanche multiplication and electron injection at the cathode are considered by Forlani and Minnaja (1964) who find that the breakdown field is proportional to $L^{-\alpha}$, where L is the specimen thickness and α lies between $\frac{1}{2}$ and $\frac{1}{3}$.

In any theory of avalanche breakdown, electrons are assumed to be field-emitted into the conduction band of the dielectric. Whether emission takes place from internal potential wells or from the cathode, its occurrence will be a rare event. The electrons are then accelerated to produce a breakdown avalanche. One will therefore expect a statistical time lag t_p between the instantaneous application of a field and the initiation of breakdown, followed by a further time lag t_f required for the formation of the discharge. Provided the initiating events occur randomly in time, the statistical time lags will be distributed according to the law $n_t = n_o \exp(-\frac{t}{\tau_p})$, where (n_t/n_o) is the relative frequency of/

frequency of time lags greater than t. The constant τ_s, which will be referred to here as the "mean statistical time lag", will decrease as the overvoltage is increased.

2.3 Collective Breakdown.

If the free electron density in a dielectric is large, breakdown may result from acceleration of existing electrons rather than from freeing of new ones by ionisation. Ionisation does not take place (at any rate in the early stages of breakdown) and is replaced by interelectronic collision as the energy loss mechanism which renders a steady state possible (cf. Section 2.2). In this thesis the term "collective breakdown" is used to include all such breakdown mechanisms.

The "high-temperature" theory of Frohlich (1947a) is of this type and refers to a dielectric containing electron traps of various depths. This theory is unusual in predicting a decrease of breakdown field with increasing temperature. The form of the dependence is

$$F_B = \text{const.} e^{\frac{\Delta V}{2kT}}, \qquad (2.7)$$

where ΔV is the depth of the shallow traps. Strictly T should be the electron temperature but it is approximately correct to use the lattice temperature. This theory was proposed as applicable to crystals at high temperatures, to impure crystals and to amorphous solids. Its application to crystals at high temperatures was qualitatively in accordance with the experimental results/

results available at the time, which showed a breakdown field increasing with temperature up to a critical temperature T_c and then decreasing with further increase of temperature (Sub-section 1.3.1). Frohlich considered that at temperatures below T_c his earlier theory of breakdown by impact ionisation applied, whereas above T_c the free electron density was sufficient to allow the collective mechanism to operate.

In a later paper (Frohlich and Paranjape 1956) a theory of collective breakdown was developed for a crystal containing no impurity levels.

No statistical time lag is predicted by the theory of collective breakdown, but Cooper and Smith (1961) have pointed out that a statistical time lag may exist since the electron density may reach its necessary high value for this mechanism only during chance fluctuations. Any formative time lag will be much shorter than in avalanche breakdown provided the free electron density is fairly uniform throughout the specimen, but in the case considered by Cooper and Smith the electron density would probably fluctuate in space as well as in time. Consequently a formative time lag would arise since free electrons would have to be accelerated to the anode from a region of high electron density before the voltage across the specimen could collapse.

The collective breakdown field, like the Zener breakdown field, is independent of specimen thickness, in contrast to the avalanche breakdown field which decreases with increasing thickness. For/

For this reason certain authors do not include avalanche mechanisms under the heading of intrinsic breakdown (O'Dwyer 1958, Frohlich and Paranjape 1956). In this thesis the more usual terminology is employed: any non-thermal mechanism that does not arise from extraneous processes is referred to as intrinsic.

2.4 Detailed Theory of Intrinsic Breakdown.

Attempts at a rigorous theoretical approach involve the solution of the Boltzmann kinetic equation with terms referring to the interaction of electrons with the field and with the lattice phonons, and to any other interactions that are to be considered. Ideally one should consider not only electron-electron interaction and ionising collisions, but also recombination processes, analogous processes involving holes, and electron injection at the cathode. In practice it is necessary to make numerous simplifying assumptions to render the solution tractable, and consequently the predicted breakdown fields are at best no more reliable than the results of the simple theories discussed in the preceding sections. In particular one of the terms referring to electronic interaction and to ionising collisions is usually neglected, so that theories refer to pure avalanche multiplication breakdown and pure collective breakdown respectively. Moreover Stratton points out that the variation of free electron density with distance along the/

the field is usually neglected. This comment was made in connection with a specific theory, that of Franz (1952), but it is generally applicable. Stratton lists other objections, but this one is particularly important in view of the experimental results indicating that the magnitude of the field strength in a dielectric near breakdown is often seriously distorted by space charges which may be electronic (Sub-section 1.3.1).

CHAPTER 3

EXPERIMENTAL.

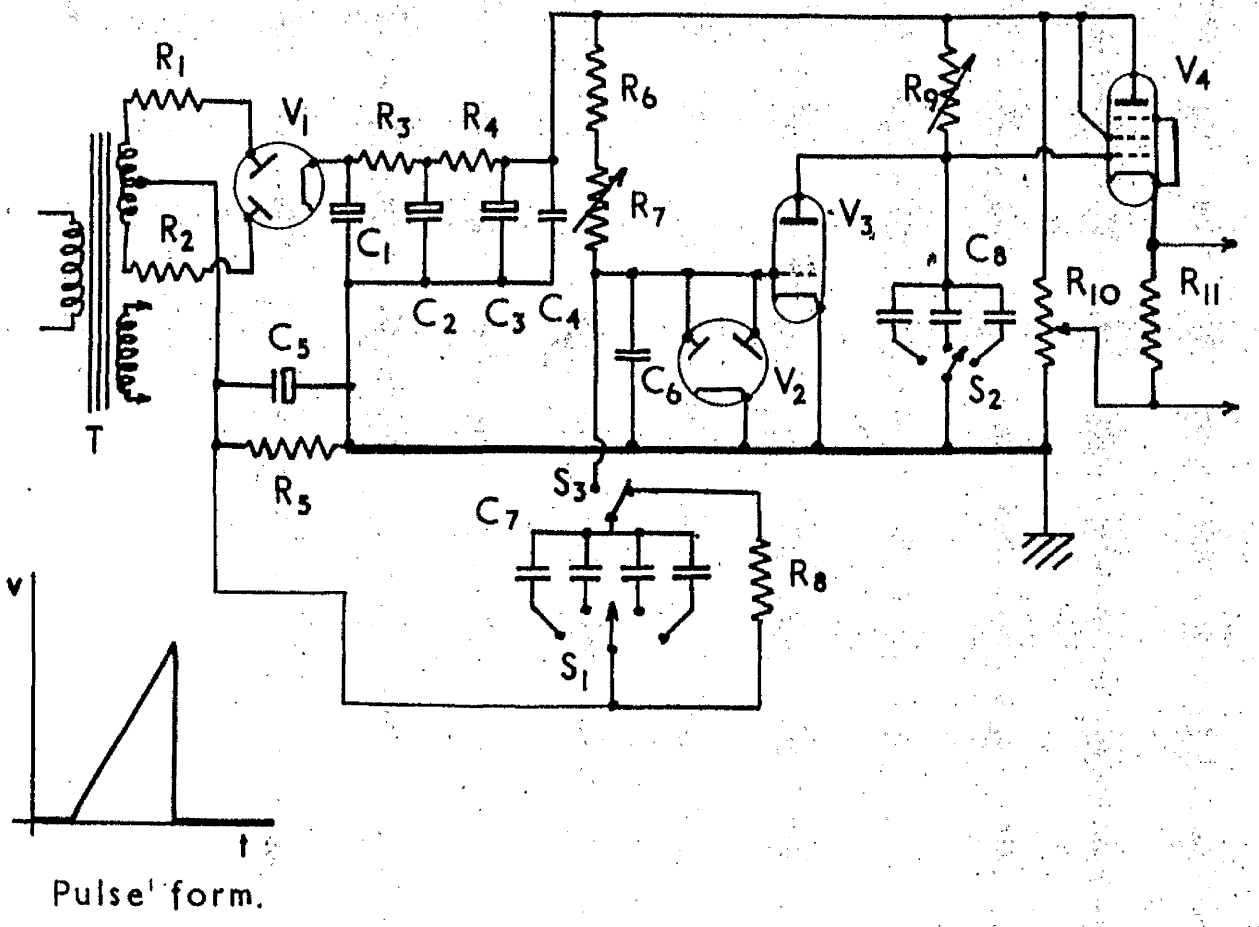
3.1 Electrical

3.1.1 Choice of electrode configuration. An aim of the work described in this thesis is to study intrinsic breakdown in dielectric films with evaporated metal electrodes. This type of electrode system introduces a risk of measuring spuriously low breakdown voltages as a result of field concentrations at the electrode edges. Recessed specimens are frequently used in bulk breakdown studies to avoid edge effects, but this is not feasible in thin films. The author has adopted an alternative method originally suggested by Saito (1936) and previously applied in thin-film measurements by Siddall (1959 - 60). Both electrodes were of evaporated metal, but the electrode edges were made diffuse so that the thickness of metal and therefore the surface conductivity would decrease towards the edges over a distance at least 100 times the dielectric thickness. Diffuse edges on the metal underlayer also ensure that at the edge of the underlayer there is no sharp step in the dielectric film and the effective minimum thickness of dielectric is not reduced.

3.1.2 Testing voltage. A finite time is required to raise any voltage from zero to its maximum value, and it is not always clear whether those previous workers who describe their results as having been obtained with "d.c." have raised the voltage rapidly, e.g./

e.g. with a switch, or more gradually as with some potentiometer arrangement. This is important since measured breakdown fields may depend on the duration of the applied voltage, and also, for this reason and because of overvoltage effects (cf. Sub-section 1.3.3), on the way in which the applied voltage varies with time.

In investigations with pulse voltages the pulse shape and duration are important for the same reasons. Two pulse shapes are widely used: square pulses, in which the voltage is increased as rapidly as possible to its final value and then kept as close as possible to this value for sufficient time for breakdown to occur, and sawtooth pulses (Fig.3.1, inset), in which breakdown occurs during the relatively slow voltage rise. Sawtooth pulses have been used by the present author. They were originally chosen since a specimen can be tested with a single pulse, the applied voltage being allowed to rise until breakdown takes place. Square pulses must be applied repeatedly and there is a risk of affecting the specimen so as to alter the breakdown voltage in attempting to measure it (Sonchik 1957). In fact evidence was obtained that no such effect occurs (Section 4.1). However the "self-healing" effect described in Section 1.1 and 4.1 enabled a large number of breakdowns to be observed within the duration of a single applied pulse. This would not have been possible with square pulses, and to obtain a comparable number of breakdowns would have been excessively time-consuming. Single-shot sawtooth pulses/



Pulse generator circuit.

Fig.3.1

pulses were therefore retained for use throughout the present investigation.

Single-shot pulses have the added advantage that the variation of the voltage across a specimen with time can be clearly seen on an oscilloscope. After preliminary investigations a Solartron Type AD 557 oscilloscope with a long-persistence phosphor was introduced to facilitate visual observation. This technique proved to be extremely useful, because information obtained from the shape of the pulse across a specimen could be used in testing further specimens on the same slide. To do this with a photographic technique would have involved intolerable delays.

The pulses were generated by a circuit (Fig.3.1) substantially similar to the one described by Plessner (1948), which gave a single voltage pulse of the shape sketched when the switch S_3 was closed. The operation of the circuit has been described by Plessner. The voltage rise rate of the output pulse can be varied with the potentiometer R_9 and the range switch S_2, while its duration can be altered by means of R_7 and S_1. The capacitor C_6 was inserted to eliminate the effects of switch bounce in S_3, which was causing the grid of V_3 to return to chassis potential for short intervals during a pulse.

The circuit as constructed suffered from certain disadvantages. The negative side of the output was not at chassis potential, but this/

this was not serious since both electrodes of the specimen under test were insulated. Switch bounce in S_3 was still indirectly a nuisance in very short pulses, whose shape could be seriously distorted by C_6, but in practice it was not found necessary to use these short pulses very often and the distortion could be tolerated.

Very slow pulses of similar shape were produced manually by scaling down the voltage of a d.c. battery with a potentiometer. Tests performed in this way would possibly have been described as "d.c." by some previous workers.

3.2 Mechanical.

One of the aims of the present work has been to extend the preliminary observations made by Weaver (1962) on the effects of moisture on the breakdown fields of thin films. It is therefore necessary to determine the breakdown voltages of films both after exposure to moisture and under dry conditions. The most convenient way of performing the measurements under dry conditions was to test freshly deposited specimens in vacuum.

The apparatus was designed so that ten specimens were deposited in each evaporation. It was therefore necessary to arrange that electrical connections could be made to any one without breaking the vacuum. The remainder of this section is a detailed description of the equipment.

The apparatus for evaporating and testing films was built on/

on top of the baseplate of the vacuum pumping unit. Photographs of this apparatus viewed from the front and from the back of the pumping unit are given in Plates 1 and 2.

The fixed Perspex disc P was mounted on top of the aluminium partition A (Plates 1 and 2), which divided the working chamber into two parts. One side was used for evaporations, the other for cleaning of the substrate in a glow discharge and for the breakdown tests. The latter side was thus shielded by the partition from the vapour streams, so avoiding electrical short circuits due to deposition of metal on the testing apparatus.

In the fixed Perspex disc were cut, on the evaporating side, the masking slots used to give the desired layout of the films, and, on the testing side, one slot through which the electrical connections were made to the specimen and another for exposing the substrate to the glow discharge for ionic bombardment cleaning.

One of the glass microscope slides used as substrates can be seen in position for cleaning in both plates. The slide S was held fixed in the carriage C by a flat spring, bearing on one end, and was clamped down by the small Perspex pieces X so that its lower surface was flush with the lower surface of the Perspex turntable T. The turntable could be rotated from a Wilson seal to bring the slide into position for each part of the evaporating and testing process in turn. The slide carriage C could be adjusted horizontally in the turntable, prior to evaporation, so permitting/

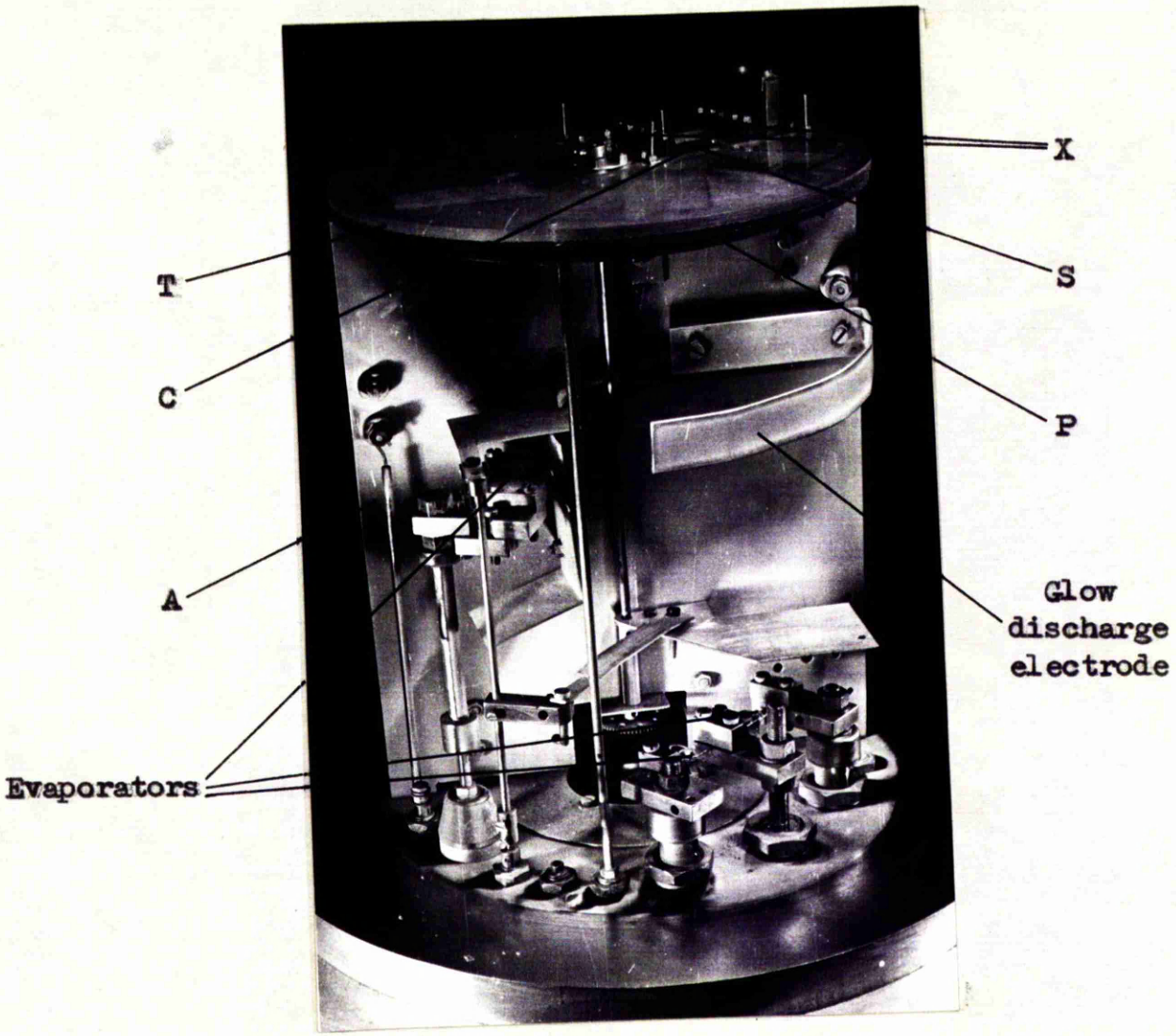


Plate 1

Working chamber of vacuum pumping unit:

evaporating side.

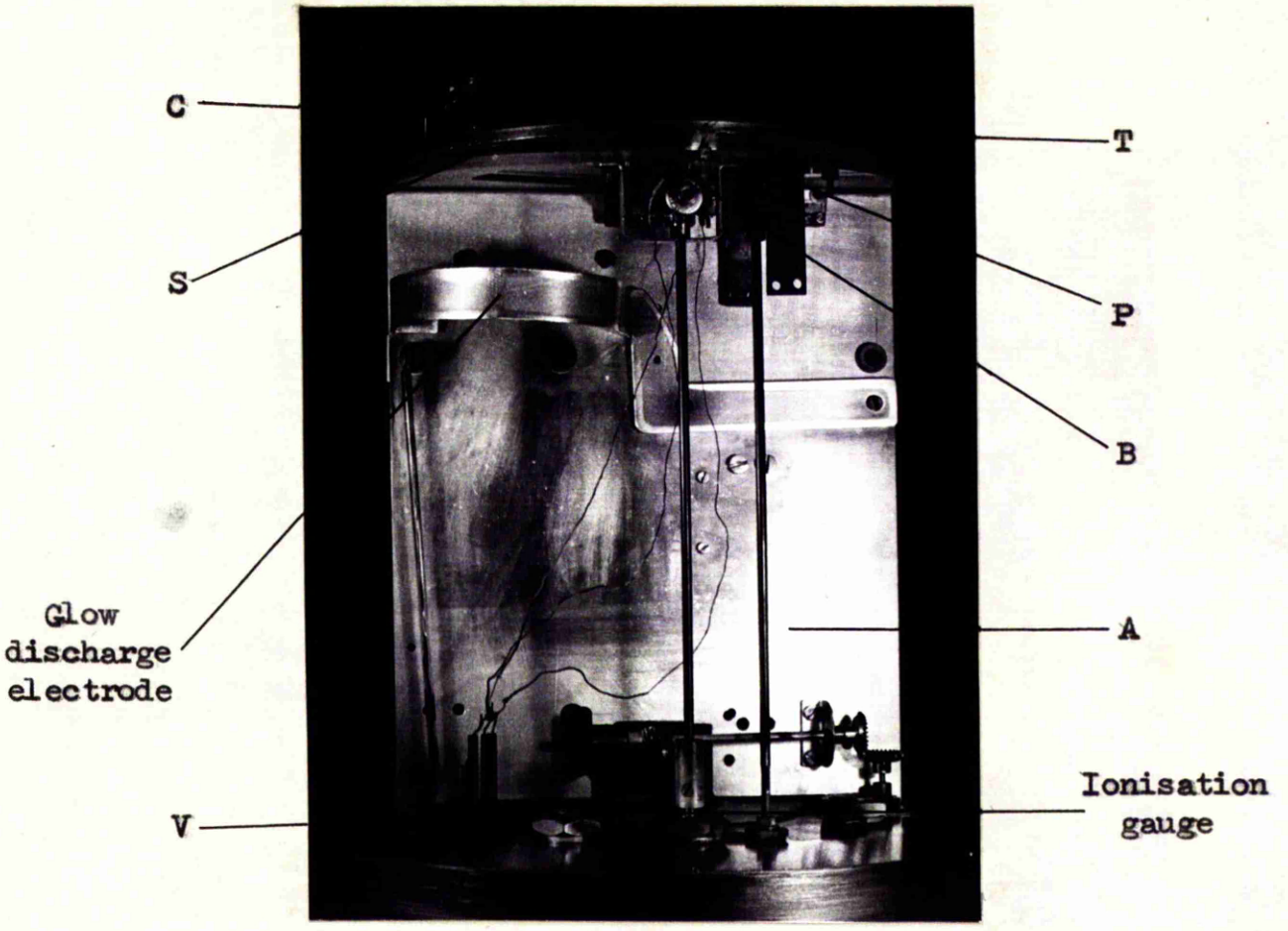
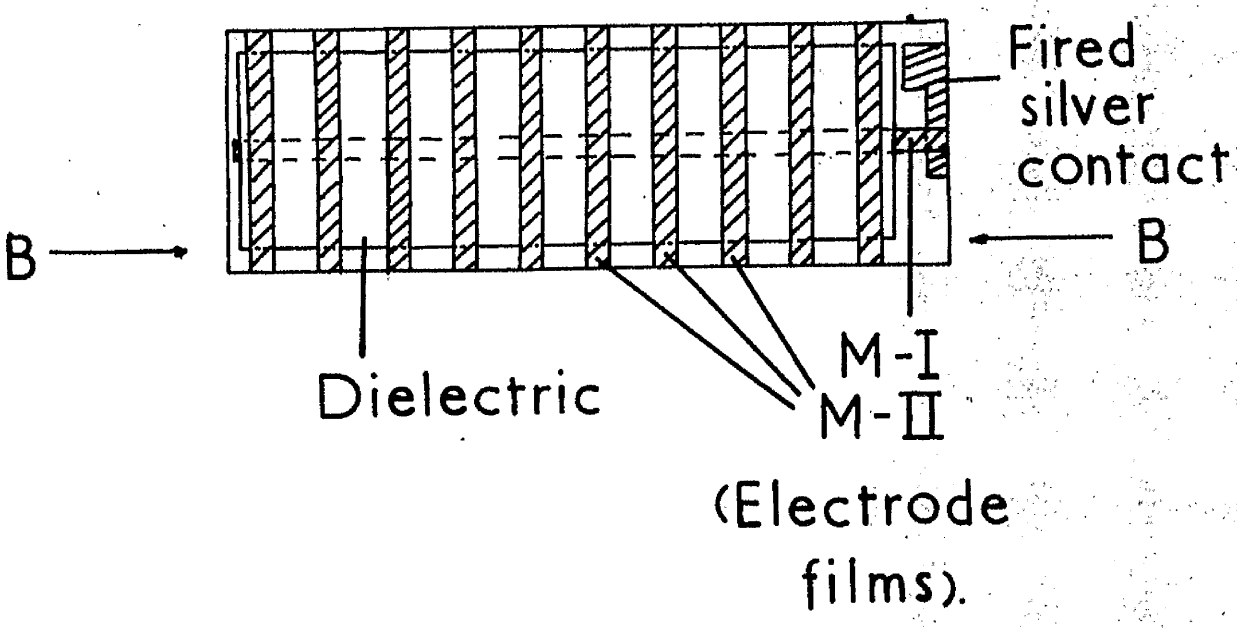


Plate 2

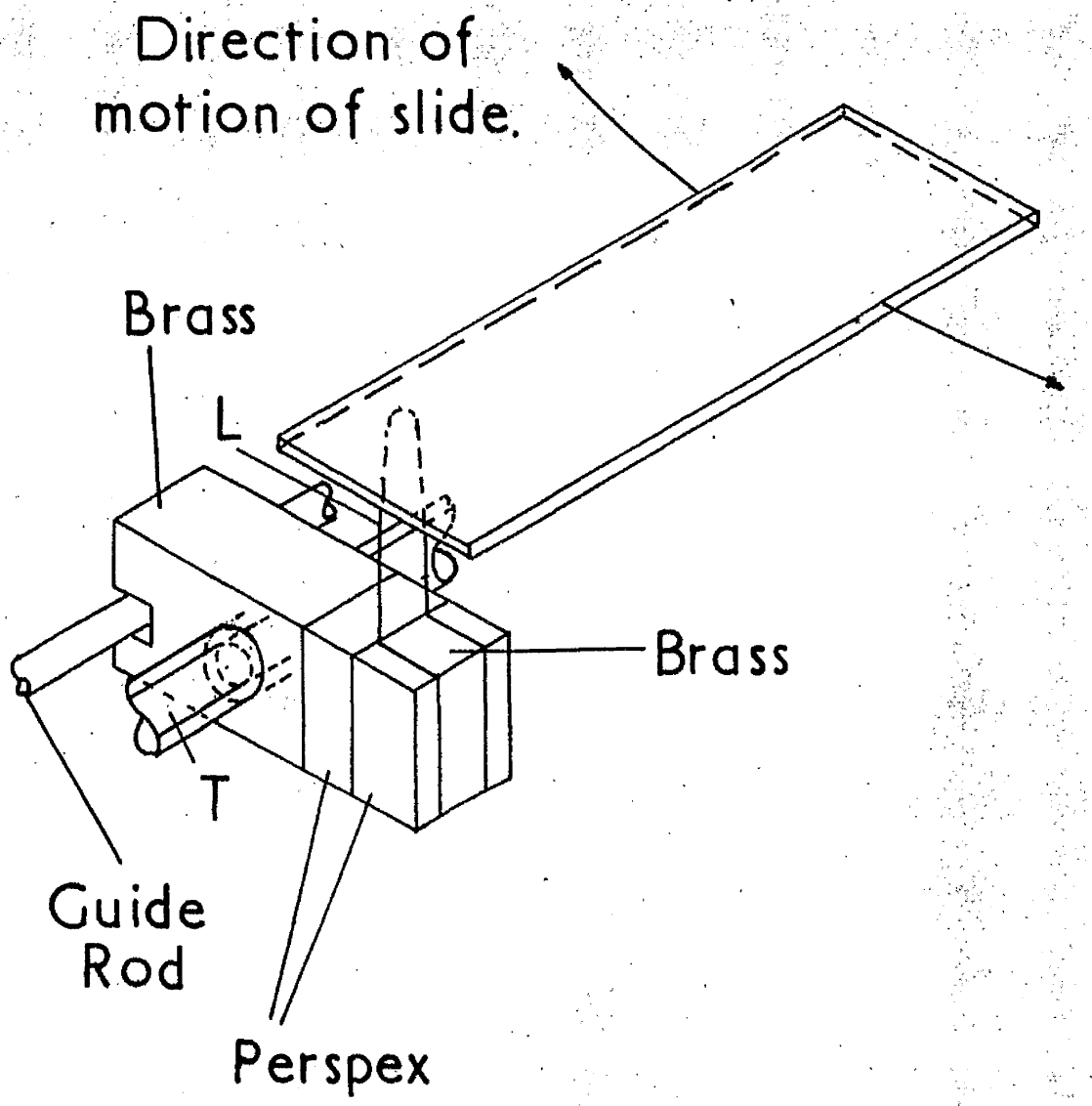
Working chamber of vacuum pumping unit:

breakdown testing side.



Arrangement of films on slide.

Fig.3.2



Testing jig (diagrammatic).

Fig.3.3

permitting a pre-set fine adjustment of the position of the slide relative to the masks.

The layout of the films on the slide was as shown in Fig.3.2, where it can be seen that the metal overlayer M-II was divided into ten strips, so that ten sandwiches for testing were formed on each slide.

The apparatus for making electrical connection to the to the specimens can be seen at B in Plate 2. A more detailed schematic drawing of it is given in Fig.3.3. The slide (shown in position for testing) could be moved in the transverse direction indicated by rotating the turntable. Contact to the slide was made by a loop L of spring steel wire which could be moved longitudinally by rotating the steel screw T (operated from a Wilson seal). The loop could thus be applied to any point on the slide. Normally it was used to make contact to one of the ten strips of the metal overlayer M-II (Fig.3.2) in order to test one of the sandwiches. Contact to the underlayer strip M-I was made by a wire soldered to the fired silver contact, which the film overlapped. The electrodes were connected to their input terminals via the vacuum-tight lead-in V (Plate 2), and both electrodes were insulated from the frame of the pumping unit.

To verify that contact effects between the loop L (Fig.3.3) and the metal film were not affecting the results, the loop was occasionally applied to the metal underlayer. A short circuit should/

should then appear across the input. The check was performed repeatedly and no resistances were detected.

All the results presented in the following chapters were obtained either with the above apparatus or with an earlier version which differed from it in construction but not in principle.

3.3 Vacuum and Evaporation Technique.

3.3.1 Apparatus. The vacuum pumping unit was of conventional type, with a Vlavac Type P2F 2" silicone oil diffusion pump backed by an Edwards Type DB 1 H rotary pump. The evaporation sources were of standard design (Holland 1956). Molybdenum boats were used for all the dielectrics and for silver, and standard tungsten basket-shaped heaters for aluminium. Holland also recommends basket-shaped heaters for the evaporation of gold, but it was found that the gold charge tended to fall through the bottom of the heater after it had melted, so that very little gold evaporated. Molybdenum boat heaters were therefore used for gold evaporation. Gold is known to attack molybdenum, but it is unlikely that serious alloying would occur provided the same heater was not used more than about twice.

The masks used to define the metal films were cut from sheet steel and attached to the fixed Perspex disc $\frac{1}{16}$" below its top surface in order to give diffuse-edged films.

The experimental procedure for the most part followed a conventional/

conventional pattern. Some details are noted in the following sub-sections.

3.3.2 Substrate cleaning procedure. Immediately before insertion into the working chamber, each slide was washed in Teepol and water, rinsed in hot running water for several minutes, dried with clean cotton wool or a clean glass cloth, and finally polished with clean lens tissue to remove dust particles. Cleaning was completed by exposing the slide to the glow discharge for 10 - 15 minutes at about 10^{-2} torr.

For some purposes in the experimental work it was considered desirable to use slides that had been selected for freedom from scratches, etc., on their surfaces. Inspection of the slides was carried out under a microscope with dark-field illumination. Since the temperature at which the silver contacts were fired on to the slides is near the range in which the glass begins to soften, there was a risk that particles of dust might become firmly attached to the slide surfaces during firing. To reduce this danger the slides were washed by the same technique as the one described in the last paragraph before the silver was painted on to them, and the firing temperature was kept down to about $400^{\circ}C$ which is below the value recommended by the manufacturers of the silver paste.

3.3.3 Evaporation pressures. The films were deposited at a starting pressure not greater than 7×10^{-5} torr, and the pressure/

pressure during evaporation did not exceed 10^{-4} torr. (Pressures in the high vacuum region were measured by an ionisation gauge connected directly to the chamber.) Each evaporation charge was pre-heated to outgas it.

3.4 Thickness Measurement.

The film thickness is required for calculation of the breakdown field. It was determined by a standard Fizeau fringe technique (Tolansky 1948). An opaque metal film was deposited over the edge of the dielectric film, and after removal from the vacuum chamber an optical flat was placed over the evaporated films and the fringe pattern formed by multiple-beam interference in the intervening air film on illumination with normally incident mercury green light was measured with a travelling microscope. It was found that satisfactory results could be obtained by arranging suitable masking so that the dielectric film terminated at BB(Fig.3.2). If a metal overlayer was then deposited across this edge the thickness could be measured.

In this technique it is essential for the edge of the film under investigation to be sharply defined. The masking slot through which the dielectric film was evaporated was therefore cut directly into the lower Perspex disc with a sharp edge at the upper surface of the disc, so that it was almost in contact with the slide when the latter was in position for depositing the dielectric.

In the course of the investigation it was found necessary to

use/

use electrodes of silver, aluminium, and gold (Chapter 4). Silver is an excellent metal for interferometric purposes since it has a high reflectivity and low absorption and contours a dielectric surface accurately (Tolansky 1948). The overlayer M-II when of silver could therefore be used in the measurement of the dielectric thickness as well as acting as an electrode. Aluminium was also found to be satisfactory for the thickness measurement and could be used for both purposes. Gold is quite unsuitable for interferometry, since it not only has a low reflectivity, particularly to green light, but also is transparent up to much greater thicknesses than silver and aluminium. An auxiliary silver film was therefore deposited and used in measuring the thickness of the dielectric film when the upper electrode was of gold.

CHAPTER 4.

DIELECTRIC TESTS ON THIN FILMS IN THE ABSENCE OF MOISTURE.

4.1 Preliminary Work.

Results were first obtained for cryolite films. Silver was chosen as the electrode metal in the hope of avoiding complications due to oxide layers, from which it is fairly free. All the films were deposited from normally incident vapour streams. The applied voltage was increased manually with a potentiometer until breakdown took place, and the breakdown voltage was measured with a voltmeter.

Short circuits between the electrodes were encountered rather frequently and only a few results, mainly for specimens of thickness between 1000 Å and 2500 Å, were obtained by this technique (Fig.4.1). The breakdown voltages lay below 5 volts, showing wide scatter and no clear dependence on thickness. This corresponds to a maximum breakdown field of about 0.5 MV/cm at 1000 Å, which seems surprisingly low since the electric strengths of ionic crystalline materials are usually about 1 MV/cm at thicknesses of the order of tenths of a millimetre and one would expect that the electric strengths would if anything increase with decreasing thickness.

A series of modifications was made in the technique in an attempt to obtain more consistent results and to account for the scatter and the low values of thos already obtained. The use of a manually controlled voltage was discontinued and tests were carried/

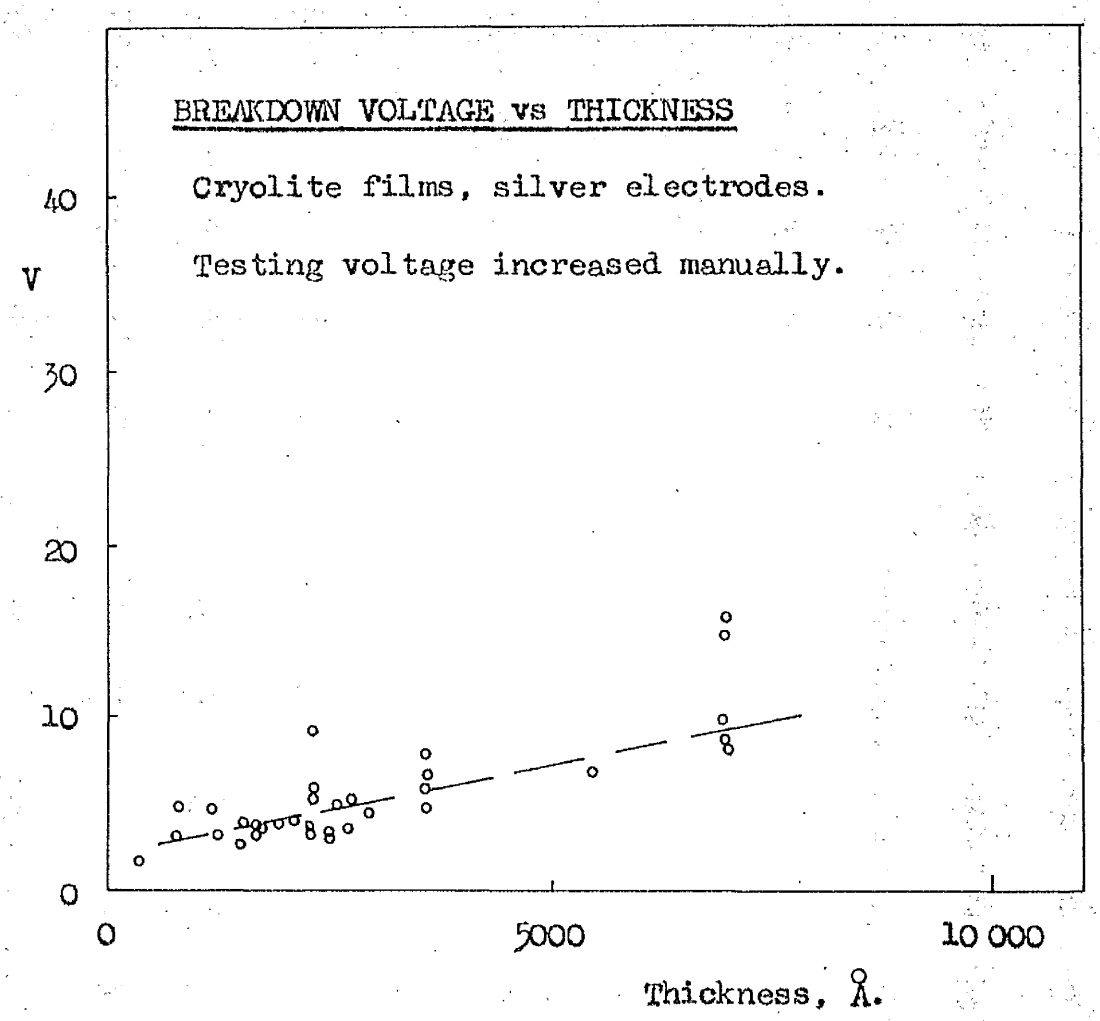

BREAKDOWN VOLTAGE vs THICKNESS
Cryolite films, silver electrodes.
Testing voltage increased manually.
V
40
30
20
10
0
0
5000
10 000
Thickness, Å.

Fig.4.1

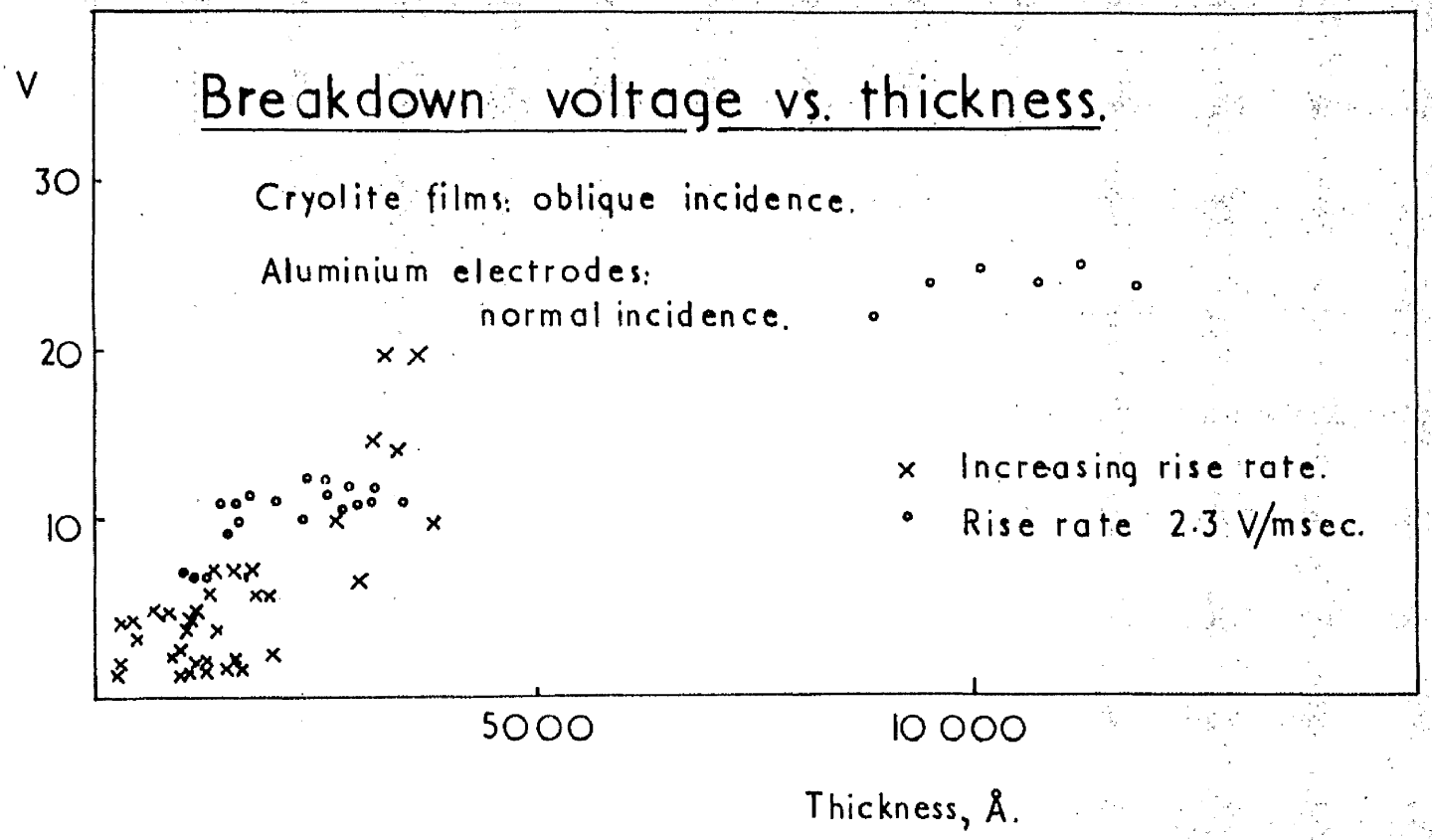
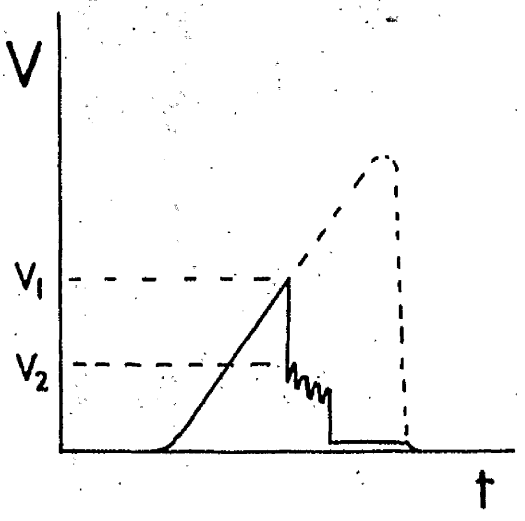
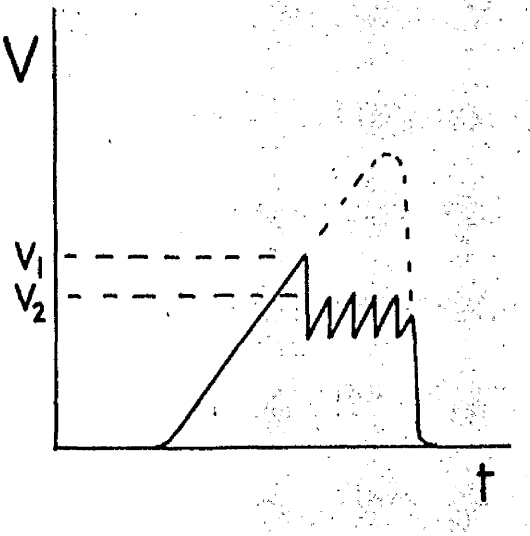

Breakdown voltage vs. thickness.
V
30
20
10
Cryolite films: oblique incidence.
Aluminium electrodes:
normal incidence.
× Increasing rise rate.
° Rise rate 2·3 V/msec.
5000
10 000
Thickness, Å.

Fig.4.2



a. Silver electrodes.



b. Aluminium electrodes.

Display on oscilloscope screen during test.

(Open circuit pulse form shown dotted).

Fig.4.3

carried out with voltages from the pulse generator described in Sub-section 3.1.2. As in the work of Plessner (1948), a series of gradually increasing pulses of equal duration was applied until the specimen broke down. The voltmeter had not given much information on the variation with time of the voltage across the specimens, and was therefore replaced by the oscilloscope with the long-persistence phosphor (Sub-section 3.1.2).

At the same time the apparatus described in detail in Chapter 3 was introduced, and the dielectric evaporator, which had previously been mounted directly below the slide, was displaced laterally from this position so that a wedge-shaped dielectric film was produced and a range of thicknesses obtained in one evaporation. The angle of incidence of the dielectric vapour stream at the centre of the slide surface was about 40°.

The results obtained by the modified technique are plotted in Fig.4.2. The electrodes were of aluminium. Silver electrodes were used at first, but so many specimens were found to be short-circuited that progress became extremely slow. This difficulty could have been caused by aggregation of the lower electrode. Evaporated silver is known to have a coarse structure, particularly when the deposition rate is low (Sennett and Scott 1950). Care was therefore taken to evaporate the silver as quickly as possible, but in spite of this precaution short circuits still occurred. The "self-healing" effect observed by Siddall (1959-60) in silicon oxide/

oxide films with aluminium electrodes (Section 1.1) suggested replacing silver with aluminium as the electrode metal. When this had been done successful results could be obtained more frequently. Short circuits could usually be removed by connecting a charged capacitor across the specimen as in Siddall's work (the present author found that a 2 μf capacitor charged to 12 volts was sufficient to burn out most short circuits.) Attempts to clear short circuits between silver electrodes in this way were nearly always unsuccessful. In addition the relative frequency of initially short-circuited specimens was much smaller with aluminium than with silver. This last advantage of aluminium electrodes was very useful since it allowed the author to confirm that the results obtained from specimens across which a capacitor had been discharged lay within the scatter limits of the results from specimens that had not been treated in this way.

The variation with time of the voltage across a specimen also depended on the electrode metal. The oscilloscope displays characteristic of silver and of aluminium respectively are sketched in Fig.4.3. Cryolite tested with silver electrodes usually exhibited a single breakdown at a voltage V_1 (Fig.4.3a). A permanent conducting path was then detected by the collapse of the voltage across the specimen. Occasionally, in thicker dielectric films, a series of repeated breakdowns occurred at lower voltages V_2 after the initial breakdown at V_1, but V_2 was usually/

usually not constant in a specimen. The breakdown voltage values plotted for silver are therefore those of V_1. When aluminium electrodes were used, on the other hand, the repeated breakdowns at V_2 were nearly always seen and gave a fairly constant voltage reading (Fig.4.3b). Except in very thin specimens, permanent breakdown did not take place until several pulses had been applied, and until then repeated breakdowns continued to occur at the same voltage V_2. The initial peak at V_1 was often not observed at all. The practice of taking the maximum observed value of V_2 for plotting in the graphs was therefore adopted. Although this decision was quite arbitrary as regards absolute magnitudes of the breakdown voltages and fields, it introduces no errors in comparing results obtained under different conditions.

The fact that repeated breakdowns could nearly always be observed when the electrodes were of aluminium is probably due to local removal of the metal from the region of the conducting path as observed by Siddall. This interpretation is supported by the appearance of the specimens after breakdown. Except when the dielectric film was very thin, aluminium electrodes exhibited markings, clearly visible to the naked eye, which on microscopic examination proved to be similar in appearance to those photographed by Siddall. When silver electrodes were used, what might have been a single marking was occasionally seen, but otherwise no evidence of breakdown was visible to the naked eye. Since initial short/

short circuits between silver electrodes usually cannot be burnt out, and since only one breakdown is usually observed in specimens with silver electrodes, it seems that the "self-healing" effect occurs much less readily with silver than with aluminium.

The constancy of V_2 suggests that the application of a voltage does not, as Sonchik (1957) suggested, affect the specimen so as to alter the breakdown field (Sub-section 3.1.2).

From Fig.4.2 it can be seen that scatter was still being encountered at this stage. Moreover the display on the oscilloscope screen was often so irregular that it was difficult to identify any breakdown voltage. In an attempt to reduce the scatter further, the technique was modified again by introducing testing with a single pulse rather than a series of repeated pulses as in Plessner's work. The longest open-circuit pulse in the range of the generator was used, so that breakdown would occur during the first pulse applied. The voltage rise rate was 14.4 V/msec (mean value over open-circuit pulse), and this value was adopted as standard. In the first few measurements a rise rate of 2.3 V/msec had been used (the results of these tests are shown together with the previous set in Fig.4.2), but unless otherwise stated all further results presented here were taken at 14.4 V/msec or at a rise rate close to this value in cases where it had been established that the small alteration did not affect the measured breakdown voltage.

The first set of results taken with single pulses is plotted in Fig.4.4/

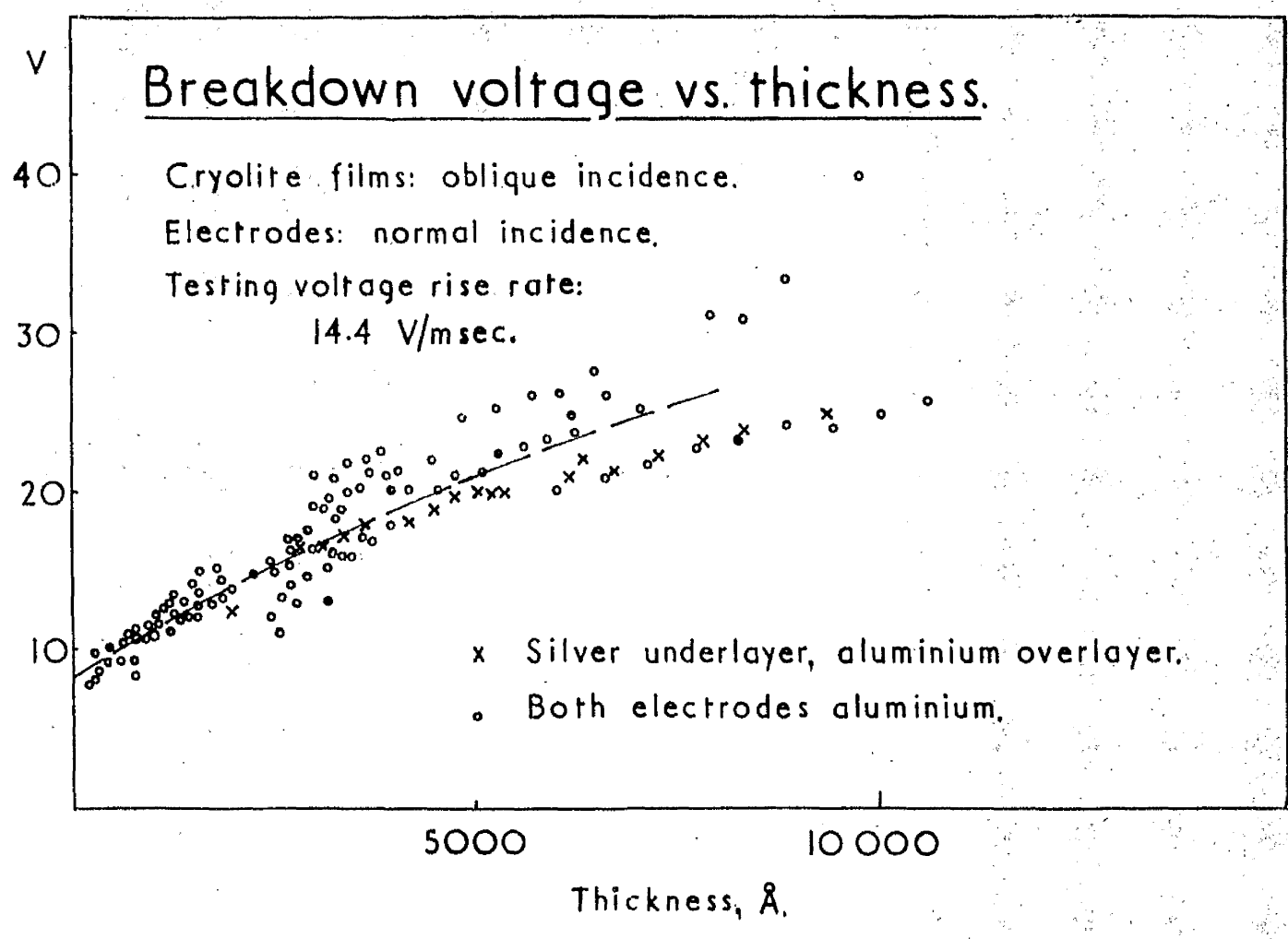

V
Breakdown voltage vs. thickness.
40
Cryolite films: oblique incidence.
Electrodes: normal incidence.
Testing voltage rise rate:
14.4 V/msec.
30
20
10
x Silver underlayer, aluminium overlayer.
o Both electrodes aluminium.
5000
10 000
Thickness, Å.

Fig.4.4

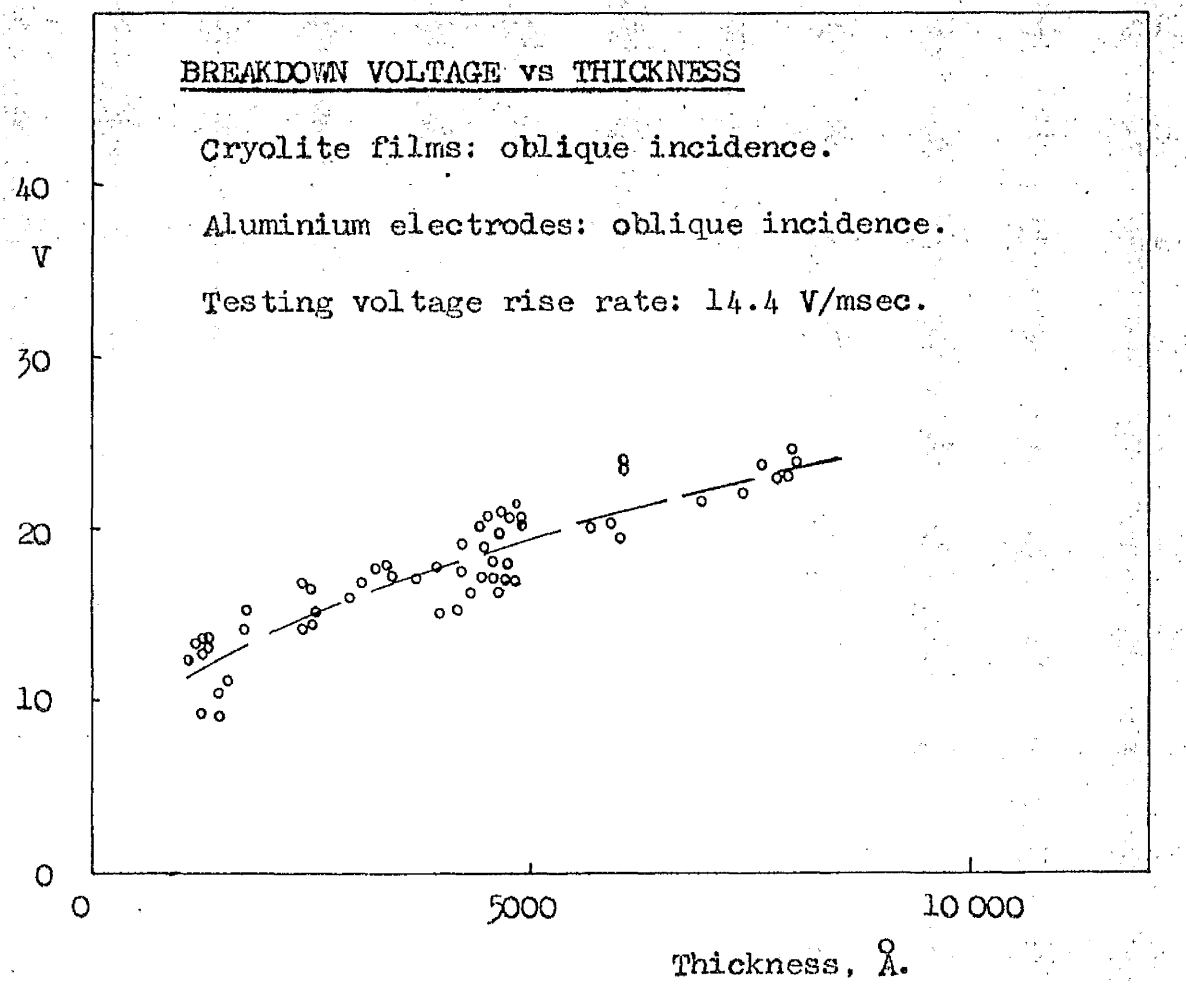

BREAKDOWN VOLTAGE vs THICKNESS
Cryolite films: oblique incidence.
Aluminium electrodes: oblique incidence.
Testing voltage rise rate: 14.4 V/msec.
40
V
30
20
10
0
0
5000
10 000
Thickness, Å.

Fig.4.5

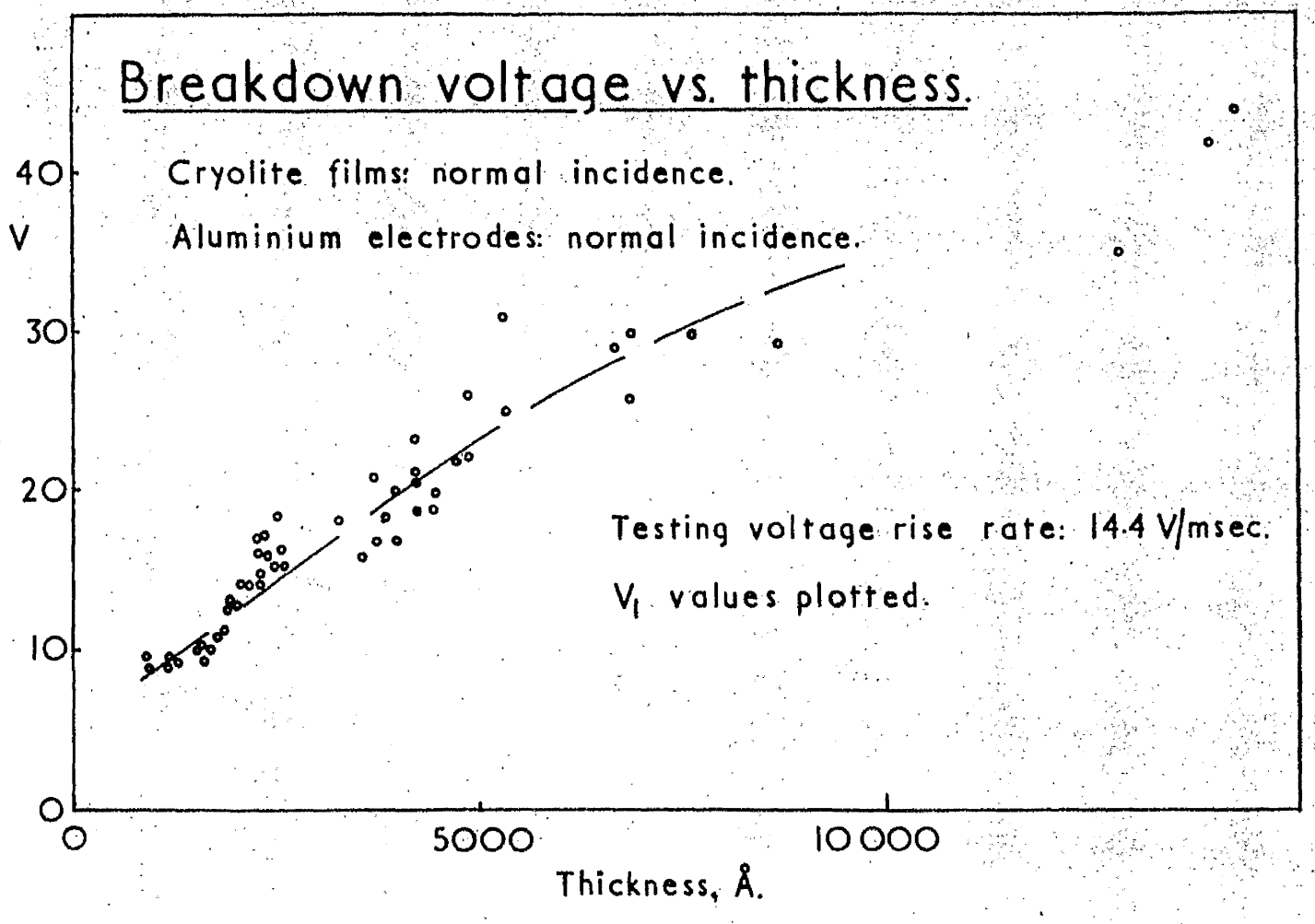

Breakdown voltage vs. thickness.
Cryolite films: normal incidence.
Aluminium electrodes: normal incidence.
Testing voltage rise rate: 14.4 V/msec.
V_i values plotted.
V
40
30
20
10
0
0
5000
10 000
Thickness, Å.

Fig. 4.6

Fig.4.4. The electrodes were of aluminium. Scatter was reduced but was still present. Some attempts were made to reduce it further. A possible cause would be penetration of the metal overlayer into irregularities in the dielectric during the deposition of the metal. One would then expect that condensing the upper electrodes from an obliquely incident atomic beam would introduce a "shadowing" effect and so reduce the depth of penetration. The lower breakdown voltage values would no longer be observed, so that the scatter would be reduced and the mean value would rise. The results of some measurements made in this way with electrodes condensed from obliquely incident aluminium vapour are plotted in Fig.4.5. The cryolite film was condensed from a normally incident vapour stream. By comparing this graph with Fig.4.3, the results for which were obtained under identical conditions except that the aluminium was condensed from normally incident vapour, it can be seen that scatter was not reduced and that the mean value is actually slightly lower at oblique than at normal incidence of the metal vapour. This effect was not studied in further detail, but the result seems to show that variations in film thickness, or at any rate short-range variations, are not important in determining the breakdown field.

Plotting values of the initial voltage peaks V_1 (Fig.4.3b) which had been observed in most of the measurements with aluminium electrodes, gave breakdown voltages (Fig.4.6) which had/

had a higher mean value but exhibited scatter within about the same limits as in the case of V_2. A final attempt at reducing scatter by evaporating and testing with drying agent (P_2O_5) in the working chamber was also unsuccessful.

Scatter thus seems to be a characteristic feature of breakdown in evaporated films as measured by the technique described here. However scatter is only to be expected in any breakdown measurements because those previous workers who have given details of this aspect of their results have usually encountered even wider scatter.

4.2 Effects of the Electrode Metal.

The presence of oxide layers on the electrodes could affect both the magnitude of the measured breakdown voltage and its thickness dependence. Oxide will almost certainly be present on the aluminium film as a result of gettering of oxygen in the residual atmosphere during and after evaporation (Brown 1961). Using aluminium electrodes could therefore lead to spuriously high breakdown fields. Oxide could also be responsible for an obvious characteristic of the breakdown voltage - thickness graph of Fig.4.4 for cryolite, namely that the mean line does not tend towards the origin but would on extrapolation cut the voltage axis at a finite value of about 10 volts. If, however, silver electrodes were used and identical breakdown fields were found, these possibilities would be eliminated.

The technique was therefore modified in various ways in an attempt to reduce the relative frequency of short circuits occurring with silver as the electrode metal. The difficulty had at first been tentatively attributed to scratches, small chips, fired-on or strongly adherent dust particles, and other irregularities on the slide surfaces. The practice of inspecting slides under the microscope before using them as substrates (Sub-section 3.3.2) was introduced, but without noticeable improvement. Even when each slide was covered with a Formvar film (by running a solution of Formvar in dioxan on to the slide surface and allowing the dioxan to evaporate) as soon as possible before inserting the slide into the vacuum chamber, only a few of the tests attempted were successful.

Silver electrodes had been used in the earliest tests and the relative frequency of successful results had been higher. For these early tests, the dielectric film had been condensed from a normally incident vapour stream. Accordingly it seemed hopeful to move the dielectric evaporator to a position vertically below the slide. When this modification had been made, the number of successful tests with silver electrodes increased sufficiently to give a working rate of progress. Since difficulty had been encountered in producing very thick dielectric films, the source-target distance was at the same time reduced from 30 cm to 15 cm, but since the earliest results had been obtained with the evaporator 30 cm/

30 cm from the slide it is not considered that the improvement was due to the shorter source-target distance. It seems likely that when the dielectric vapour was obliquely incident small areas had been shielded from the vapour stream by irregularities such as dust particles on the surface of the slide. Thus when the overlayer was evaporated it would make direct contact to the lower electrode in these "shadows". Alternatively the angle of vapour incidence may affect the structure of the film. It has been shown that metal films deposited near grazing incidence are composed of unusually large aggregates (Koenig and Helwig 1950, Holland 1953). If a similar effect occurred in dielectrics at the comparatively small angles of incidence used here, short circuits might be formed in the gaps between the crystallites at larger thicknesses than when the dielectric was deposited from normally incident vapour. In either case it would be possible to burn out the short circuits if the electrodes were of aluminium but not if they were of silver.

The breakdown voltages measured by this technique are plotted against thickness in Figs.4.7 and 4.8 for cryolite films with electrodes of silver and aluminium respectively. Using silver electrodes has given results about 40% lower than those obtained with aluminium. The magnitude of the breakdown fields could therefore have been affected by oxide on the aluminium. The fact that silver and aluminium electrodes give a similar thickness/

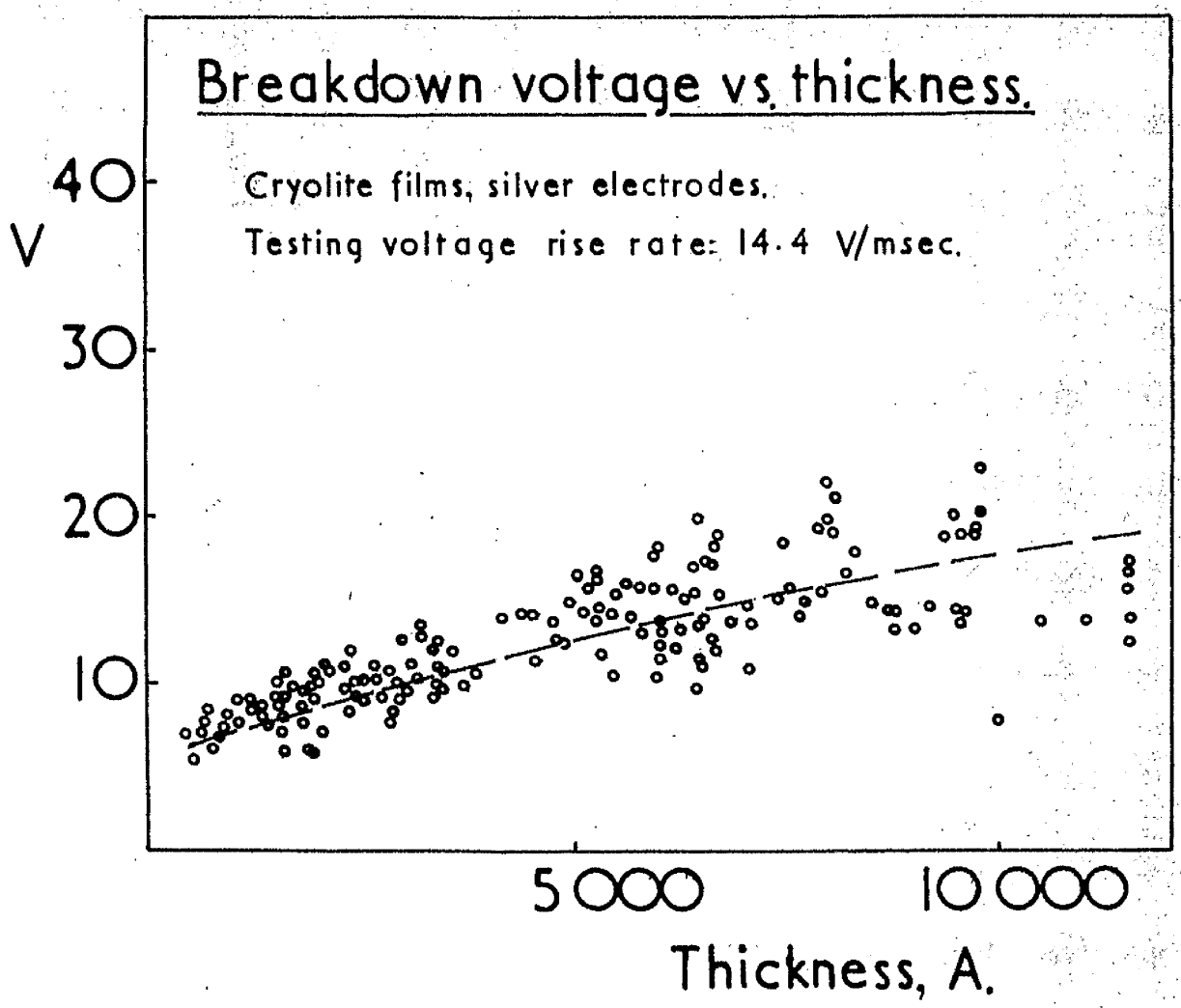

Breakdown voltage vs. thickness.
Cryolite films, silver electrodes.
Testing voltage rise rate: 14.4 V/msec.
V
40
30
20
10
5000
10000
Thickness, A.

Fig.4.7

BREAKDOWN VOLTAGE vs THICKNESS

Cryolite films. Testing voltage rise rate: 14.4 V/msec.

Electrodes:

- ∘ Both aluminium, overlayer +ve.
- ▿ Both silver, overlayer -ve.
- \+ Aluminium underlayer +ve, silver overlayer -ve.
- × Silver underlayer +ve, aluminium overlayer -ve.

All films deposited at normal vapour incidence.

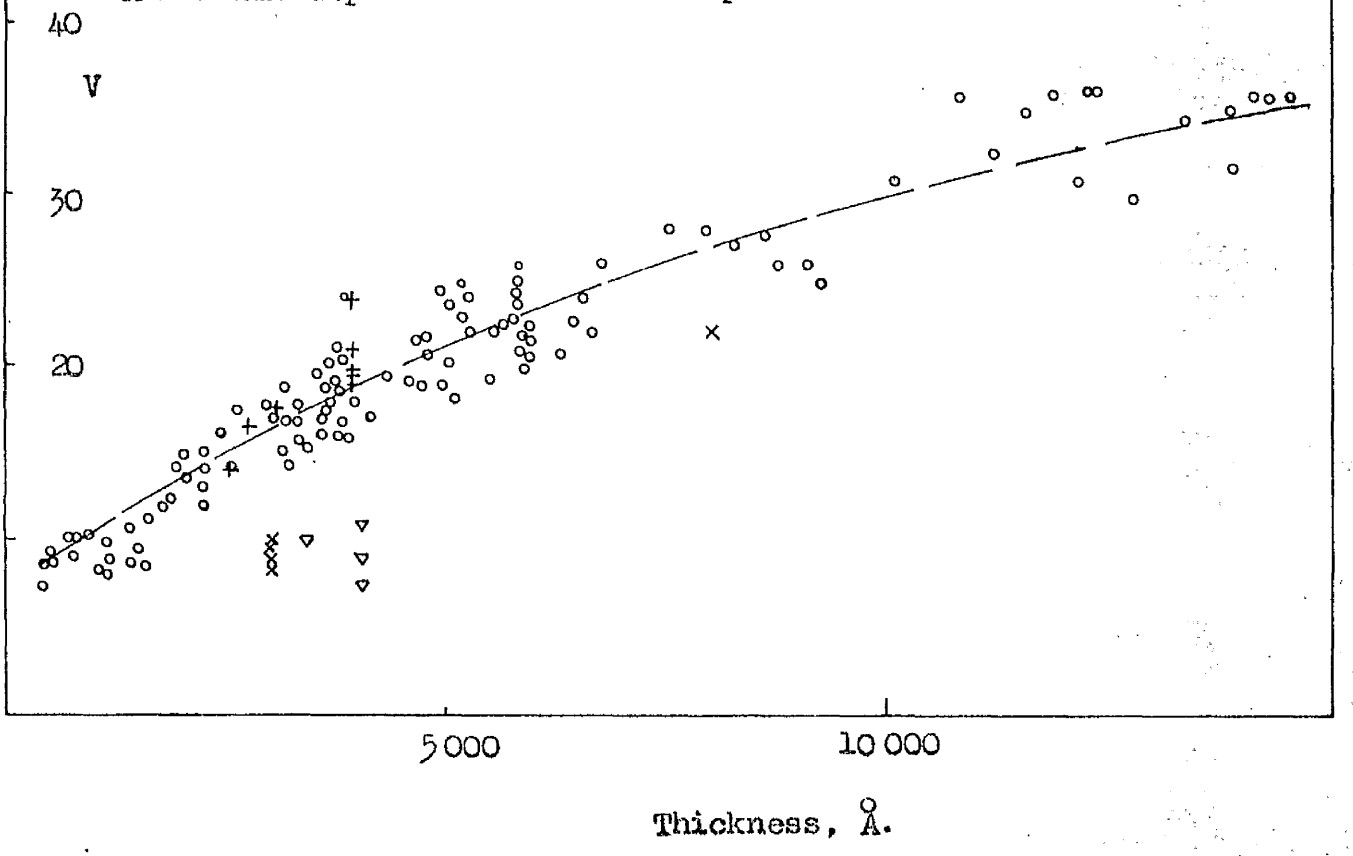


Fig.4.8

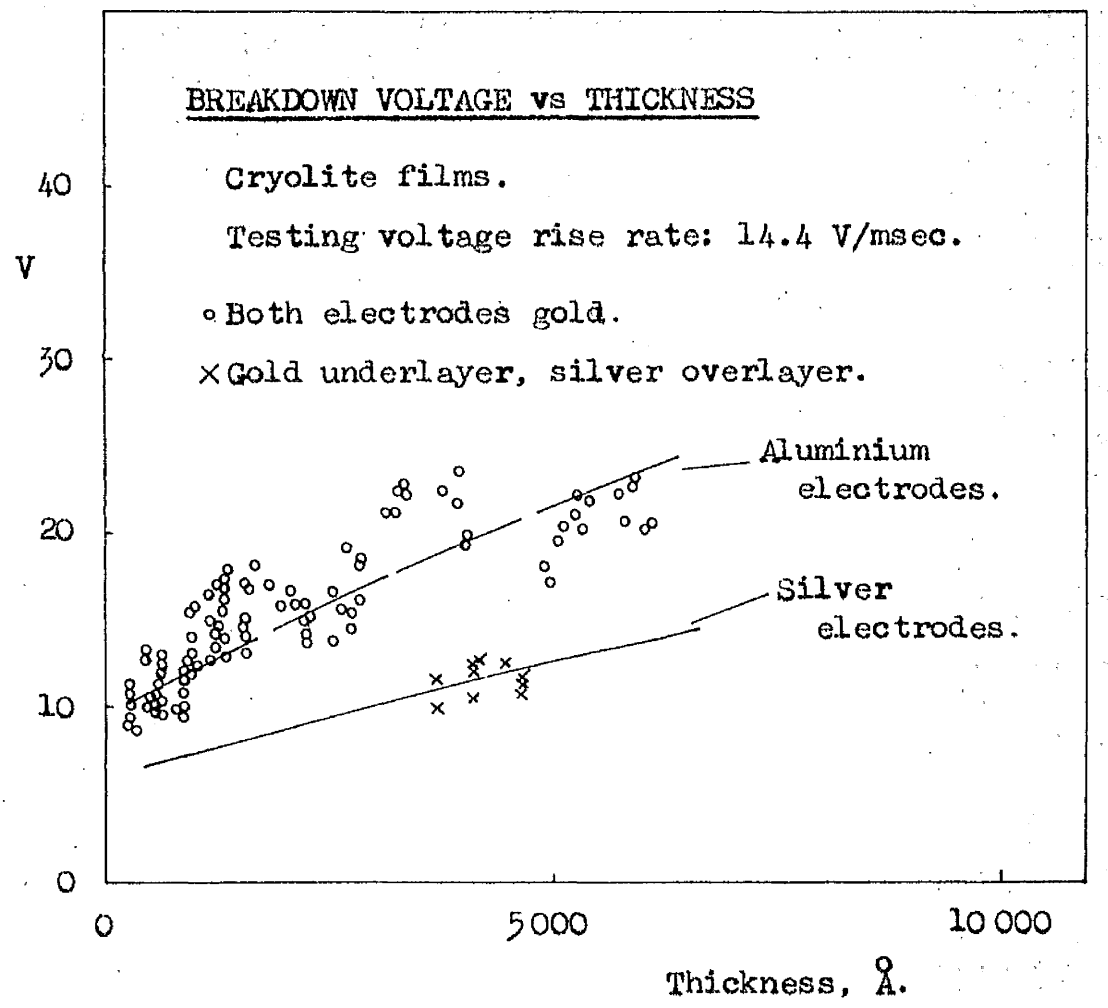

BREAKDOWN VOLTAGE vs THICKNESS
Cryolite films.
Testing voltage rise rate: 14.4 V/msec.
∘ Both electrodes gold.
× Gold underlayer, silver overlayer.
Aluminium electrodes.
Silver electrodes.
V
40
30
20
10
0
0
5000
10 000
Thickness, Å.

Fig.4.9

thickness dependence suggests at first sight that oxide layers have not qualitatively affected this aspect of the results. In particular it might seem that the finite breakdown voltage found even with silver electrodes on extrapolating to small thicknesses cannot be due to oxide. However Benjamin and Weaver (1961) in the course of measurements of adhesion of evaporated metal films to glass, have shown that some oxide may be present even on a silver film.

The measurements of Benjamin and Weaver revealed no evidence of oxide on evaporated gold films. Tests were therefore performed on cryolite films with gold electrodes. The results are plotted in Fig.4.9. For reference, the mean lines of the corresponding graphs for silver and aluminium electrodes (Figs.4.7 and 4.8) are also included. To within the scatter limits, the results taken with gold electrodes are indistinguishable from those with aluminium.

This surprising result implies immediately that oxide layers on the aluminium are not measurably affecting the variation of breakdown voltage with thickness and are not responsible for the discrepancy between the results with aluminium and silver electrodes.

Gold and aluminium electrodes resembled each other in a number of other ways and differed from silver. Initial short circuits were much less common in specimens with gold or aluminium electrodes than in those with silver, and could often be cleared by/

by discharging a capacitor across the specimen. The display on the oscilloscope screen when gold electrodes were used was similar to the one associated with aluminium electrodes and sketched in Fig.4.3b (except that the initial voltage peak V_1 was usually not seen), and gold electrodes after testing showed breakdown markings similar to those seen in the aluminium films. These observations together indicate that "self-healing" as observed by Siddall with aluminium electrodes also occurred with gold although not with silver.

Further information on the behaviour of these electrode metals was obtained from some measurements with one electrode of aluminium and the other of silver. Some results are included in Fig.4.4. Provided the upper electrode was the positive one, the results were characteristic of the overlayer metal in value, in the relative frequency of initial short circuits, and in the readiness with which "self-healing" occurred. Subsequently some tests were made with one silver and one aluminium electrode but with the overlayer now negative. The results, which are included in Fig.4.8, were now characteristic of the underlayer metal. In other words the results were always characteristic of the positive electrode whether it was the underlayer or the overlayer. A few measurements were made on cryolite with one silver and one gold electrode, and the results (included in Fig.4.9) were consistent with this conclusion.

These/

These observations can obviously not be explained by internal field effects due to the different work functions of dissimilar metals (Simmons 1963), because a reduced value of breakdown voltage was measured even when both electrodes were of silver. However the electrode work functions could also affect the breakdown fields if the latter depended on electron emission at the cathode. On the other hand the "preferred values" of work function of silver, aluminium, and gold quoted in the "Handbook of Chemistry and Physics" (1961 - 62) are respectively 4.73 eV, 4.03 eV, and 4.82 eV. There is considerable disagreement between different authors as to the values of work function, but one would expect them to be qualitatively correct in suggesting aluminium rather than silver as the unique metal. In any case the results show that the anode is the important electrode in determining the breakdown field, and any effect at the cathode has been too small to be detected.

Another possible cause of the low breakdown fields measured with silver electrodes would be a difference between the structures of the metal films, but it is known that aluminium films have a fairly continuous structure while gold is more aggregated than silver (Benjamin and Weaver 1961). Moreover one would expect that the results would be characteristic of the underlayer metal (or possibly the overlayer), whereas in fact they are/

are characteristic of the anode whether it is the underlayer or the overlayer.

Thus none of these suggestions is capable of accounting for the observed electrode effects. The most probable explanation seems to be one in terms of migration of silver positive ions under the action of the applied field. It is known that in a strong field dendrites of metallic silver, extending into the dielectric from the anode, are formed (Kohman et al. 1955, Balygin 1960). The testing voltage would thus appear across an effectively reduced thickness of dielectric, and local field concentrations would probably arise. This suggestion is consistent with the fact that the anode is the important electrode, and unlike those previously discussed would also account for the large number of initial short circuits between silver electrodes and the fact that "self-healing" does not readily take place.

Since the voltage was applied only for times of the order of a millisecond it might seem that an unduly high mobility would have to be assigned to the silver ions. It is difficult to comment quantitatively in the absence of published data on mobility of silver under these conditions, and indeed of studies of silver migration under uniform fields. Balygin (1960), studying silver migration in certain Soviet synthetic ceramics, used a roughly radial field and found that silver would migrate over/

over the whole radial distance between the electrodes, which appears to have been approximately 40 mm, in about 20 hours at 400°C when the applied voltage was 2kV. The mean field strength was thus about 500 V/cm and the mean ion drift velocity about 2mm per hour, i.e. about 5×10^{-5} cm/sec. This gives a mobility of about 10^{-7} cm^2/volt sec. At a field strength of 1 MV/cm this mobility would give a velocity of 0.1 cm/sec. With pulses of the type used in the present investigation the voltage would not be applied for the total duration of the pulse, but to a first approximation it may be taken to have been applied for about a tenth of the pulse duration - say 0.5 msec. In this time the silver would migrate 5000 Å if it moved at the velocity just calculated.

The above is of course only a very rough estimate, but since there is no published indication of the activation energy, which would in any case probably depend on the material over which the silver was migrating, the velocity at room temperature could lie within wide limits and it is quite unnecessary to be more precise. Provided that the activation energy is low enough and that the mobility increases with field strength, it is reasonable to suggest that silver could migrate a sufficient distance, even at room temperature, to give a noticeable reduction in the breakdown field.

If this explanation is correct, then the behaviour of silver electrodes/

electrodes under strong fields is anomalous and one may take the results with gold or aluminium electrodes as typical. Hence it was convenient to use these electrode metals in breakdown tests on dielectrics other than cryolite. Aluminium, being much the cheaper of the two metals, was normally used, but it suffers from a disadvantage from which gold is fairly free. At the edge where it overlapped the fired silver contact, the aluminium film on the glass tended to become separated from the silver by some form of lateral diffusion to give an open circuit. The process appears to be accelerated by the presence of moisture. In the work on dry specimens, open-circuiting of this kind could be tolerated since it did not occur very often.

In passing it may be noted that there is no significant difference between the mean lines of Figs.4.4 and 4.8 although these graphs refer to angles of dielectric vapour incidence in the regions of 40° and 0° respectively. Thus the breakdown field does not depend on the angle of incidence. This incidentally implies that variation over a slide of the direction of vapour incidence does not contribute to the scatter in the results.

4.3 Results for Films of Cryolite, Lithium Fluoride, and Sodium Chloride.

It is clear from the discussion in the last section that the finite breakdown voltages (about 10 volts for gold or aluminium electrodes/

electrodes) found on extrapolating to small thicknesses the breakdown voltage graphs for cryolite cannot be due to oxide on the metal films or to any effect of their work functions or structure. However the graphs may turn towards the origin at thicknesses below those for which results are available. Attempted measurements on very thin dielectric films were frequently short-circuited, but care was taken to extend the range of measurements to the smallest possible thicknesses. The slides to be used in these tests were selected after microscopic examination, and large numbers of specimens were tested in order to yield a sufficient number of results in spite of short circuits. Even with these precautions, no successful results were obtained on specimens thinner than about 500 Å.

No measurements on electric breakdown in cryolite have been seen in the literature, and the complicated structure of this substance makes it extremely difficult to calculate an electric strength on the basis of any breakdown theory. Lithium fluoride and sodium chloride were therefore investigated (the reasons for choosing these substances were stated in Section 1.5). The technique was the one decided on in the light of the preliminary experiments with cryolite: all films were deposited from normally incident vapour streams, the source-target distance being about 15 cm for the dielectrics and 30 cm for the metals, and unless otherwise/

otherwise stated the breakdown tests were performed with a single sawtooth pulse of rise rate about 14 V/msec. The standard electrode metal was aluminium.

Short circuits were frequent in sodium chloride specimens. Moreover each evaporation charge of this material had to be outgassed for one or two hours to get rid of all moisture, whereas a period of ten to fifteen minutes was sufficient with the insoluble dielectrics. Consequently the rate of progress with sodium chloride was rather slow. Only sufficient results have therefore been obtained to verify that the behaviour of this material was qualitatively similar to that of the other dielectrics and to give an indication of the magnitude of the breakdown field. Gold was used as the electrode metal in some of the tests on sodium chloride since short circuits seemed to occur rather less frequently than with aluminium.

The results are plotted in Figs.4.10 and 4.11. These graphs resemble the corresponding one for cryolite (Fig.4.8) in that the mean lines tend to finite breakdown voltages on extrapolation to small thicknesses.

4.4 Effect of Testing Voltage Rise Rate.

In the early results obtained by applying a manually increased voltage to cryolite specimens (Section 4.1), the results were lower than those for specimens tested at 14.4 V/msec and exhibited wider scatter. Observations of this kind could well give/

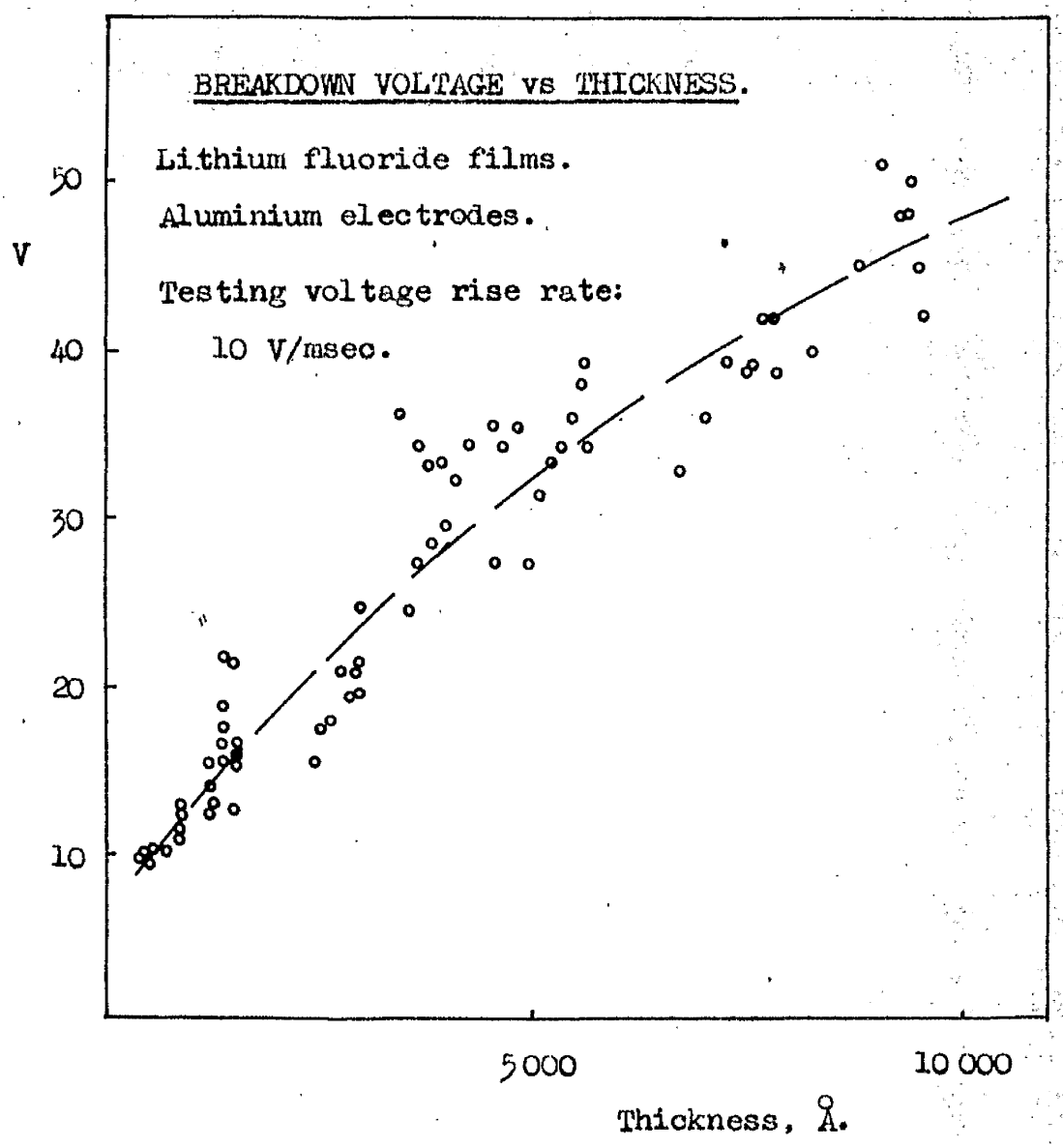

BREAKDOWN VOLTAGE vs THICKNESS.
Lithium fluoride films.
Aluminium electrodes.
Testing voltage rise rate:
10 V/msec.
V
50
40
30
20
10
5000
10 000
Thickness, Å.

Fig.4.10

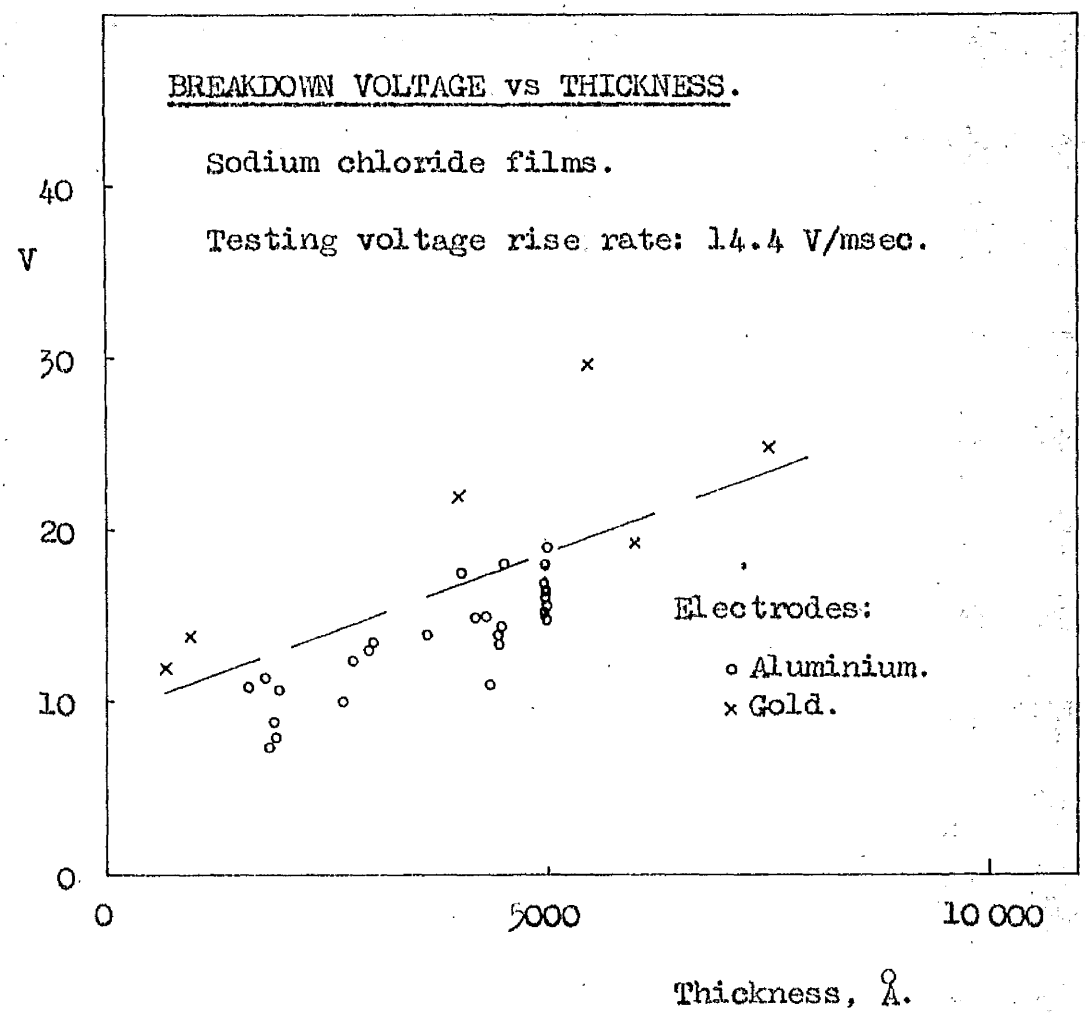

BREAKDOWN VOLTAGE vs THICKNESS.
Sodium chloride films.
Testing voltage rise rate: 14.4 V/msec.
V
40
30
20
10
0
0
5000
10 000
Thickness, Å.
Electrodes:
o Aluminium.
x Gold.

Fig.4.11

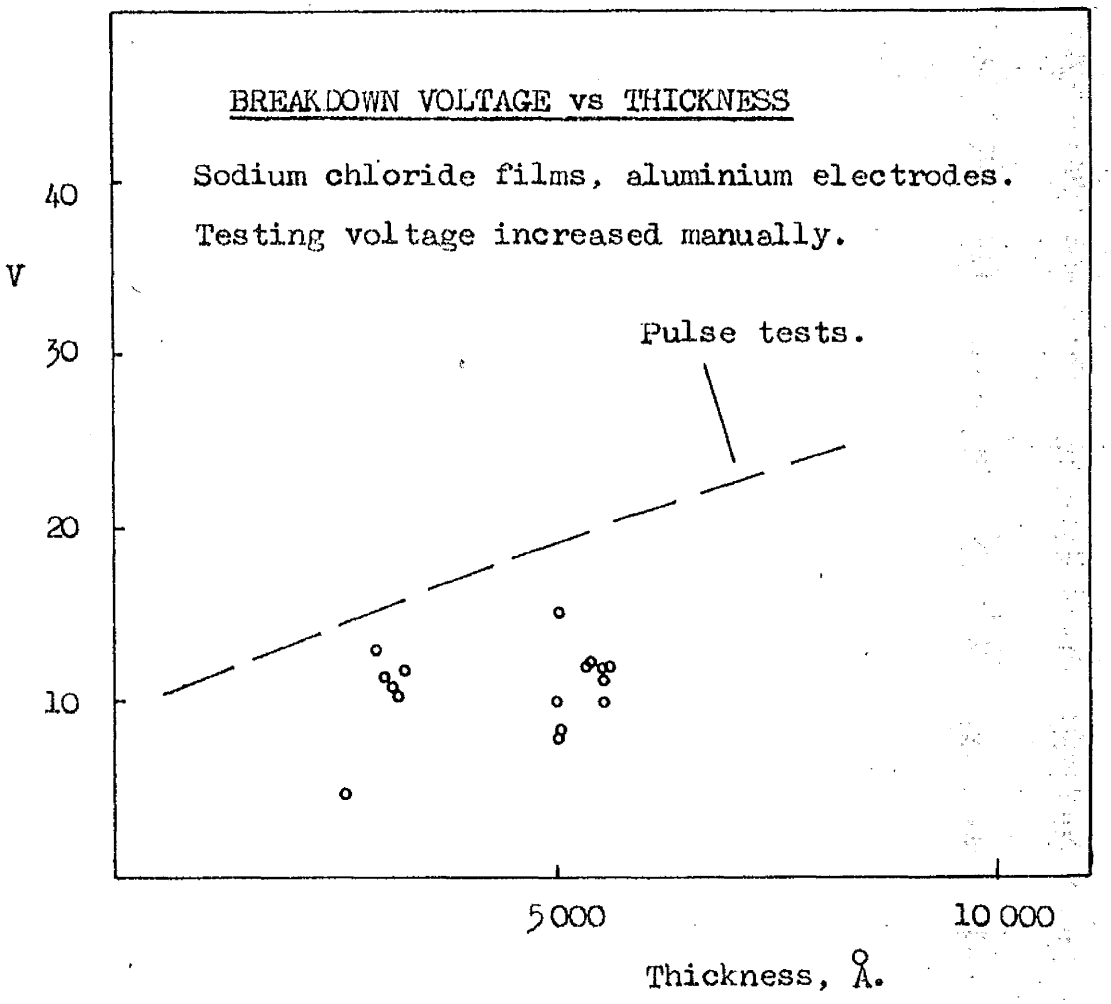

BREAKDOWN VOLTAGE vs THICKNESS
Sodium chloride films, aluminium electrodes.
Testing voltage increased manually.
Pulse tests.
V
40
30
20
10
5000
10 000
Thickness, Å.

Fig.4.12

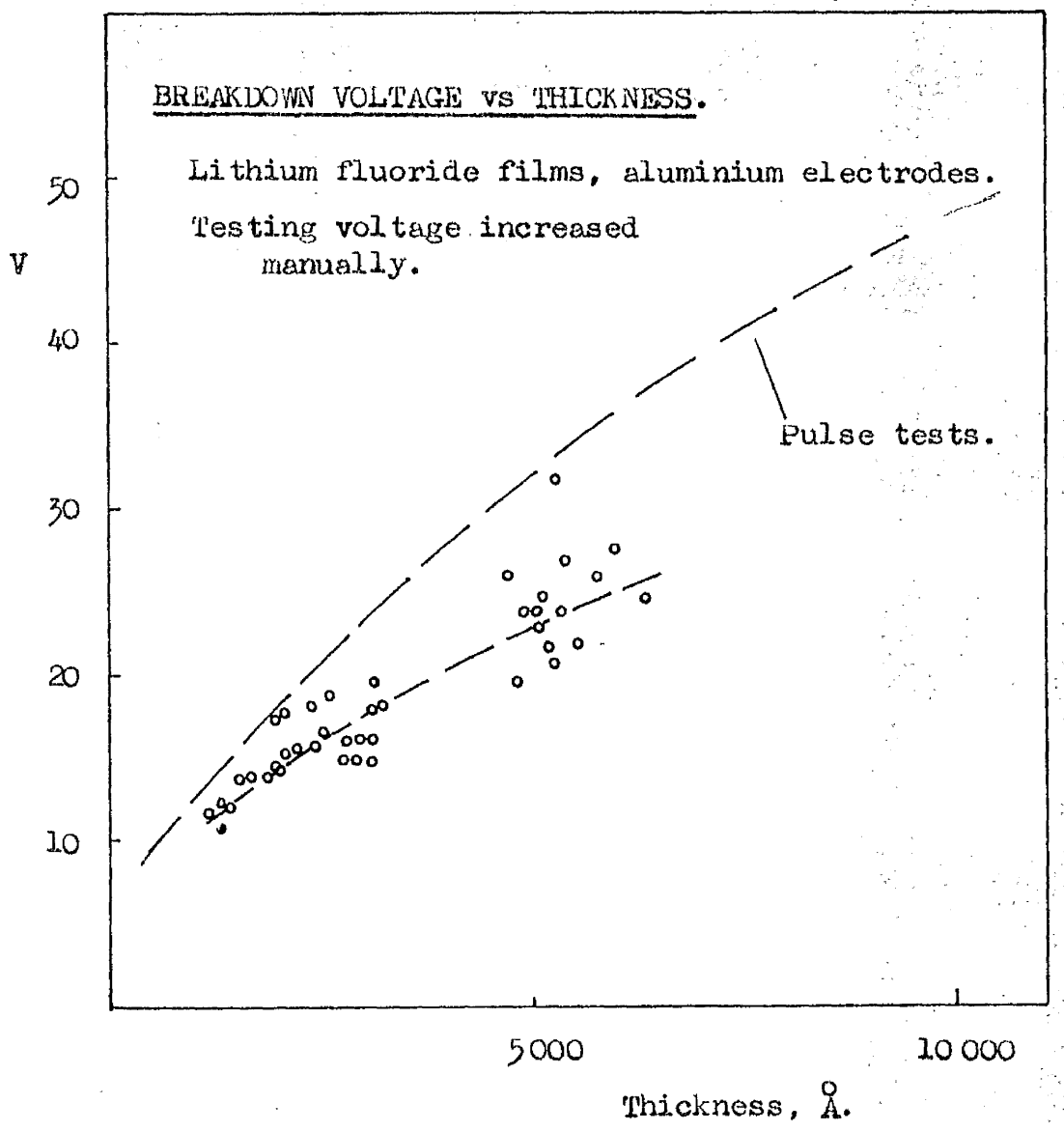
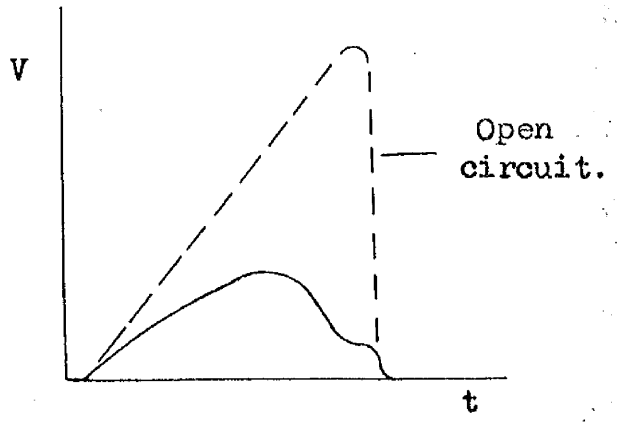

BREAKDOWN VOLTAGE vs THICKNESS.
Lithium fluoride films, aluminium electrodes.
Testing voltage increased manually.
Pulse tests.
V
50
40
30
20
10
5000
10 000
Thickness, Å.

Fig.4.13



Oscilloscope display for low testing voltage rise rate.

Fig.4.14

give useful information on the breakdown mechanism and it was desirable to find whether a similar effect occurred in the other dielectrics.

Films of sodium chloride and lithium fluoride were therefore prepared and tested with a manually increased voltage. The long-persistence oscilloscope was used at the maximum setting of the timebase scanning time (6 sec) so that the variation of voltage across the specimen could easily be studied. The voltage rise rate was about 0.01 V/msec.

The breakdown voltages are plotted against thickness in Figs.4.12 and 4.13, and the mean line for the corresponding tests at about 14.4 V/msec is shown with each set of results. In each case the results lie below the mean line for the pulse tests.

The display on the oscilloscope screen showed that the voltage across a specimen usually varied in essentially the same way as in the pulse tests, remaining indistinguishable from the open-circuit value until the breakdown voltage was reached, after which breakdown pulses alternating with "self-healings" were observed. Occasionally, in cryolite specimens, the display gave evidence of a large pre-breakdown current, beginning at the start of the pulse, and the voltage across the specimen fell off gradually instead of collapsing suddenly. A display of this kind is sketched in Fig.4.14.

The fact that the breakdown voltage is lower in those "manual" tests/

tests suggests some dependence of electric strength on pulse duration of the same kind as the one reported by Plessner (1948), who found that the breakdown voltage of a thin film increased as the duration of the applied pulse was reduced. On this basis one would expect that when, as in the present investigation, specimens are tested at a constant voltage rise rate rather than a constant pulse duration, the breakdown voltage would increase with the rise rate. To investigate this possibility, tests were performed on a series of cryolite specimens of thickness 3500 ± 500 Å and on another series of thickness 9500 ± 500 Å. Provided the thickness is kept within these limits, Fig.4.8 shows that the variation in breakdown voltage resulting from variation in thickness is not appreciable. Aluminium electrodes were used throughout. To eliminate any effect of variation over a particular slide of the angles of incidence of the vapour streams, of variation of the evaporation conditions from slide to slide, etc., tests at all the different rise rates were performed on each slide, and it was arranged that corresponding sandwiches on different slides would be tested at different rise rates.

The results showed that any dependence of breakdown field on pulse duration was within the scatter limits. A large number of measurements had therefore to be made at each rise rate. The results are plotted in Fig.4.15 in the same form as Plessner plotted his results, namely that of a graph of breakdown field against the time/

time interval from the start of the applied pulse to breakdown. The mean of the values obtained at each pulse duration is plotted plus or minus the standard deviation.

Plessner's observation of an increase in breakdown field with decreasing pulse duration appears to be confirmed. However the variation is within the scatter limits and could be due to the same causes as the scatter. A significance test was therefore applied to each of the two sets of results. The probability that the observed variation is due to chance was found to be about 0.1% for the specimens 3500 ± 500 Å thick and well below 0.1% for the specimens 9500 ± 500 Å thick. The calculations involve only routine statistical techniques and are therefore given in the following appendix.

4.5 Appendix: Significance Tests.

Fig.4.15 shows that any correlation between the breakdown field F_B and the logarithm of the pulse duration t_{ap} is approximately linear. It is therefore legitimate to calculate the correlation coefficient r and apply the "t" test provided F_B and log t_{ap} are used as variables. In fact the breakdown voltage V_B has been used instead of F_B as the y variable. This merely introduces a constant factor (the specimen thickness) and does not affect the validity of the calculation. As the x variable the logarithm of the voltage rise rate $\frac{dV}{dt}$ has been used. This is legitimate, because since $\frac{dV}{dt} \simeq$ constant $\simeq V_B/t_{ap}$ and since the

variation/

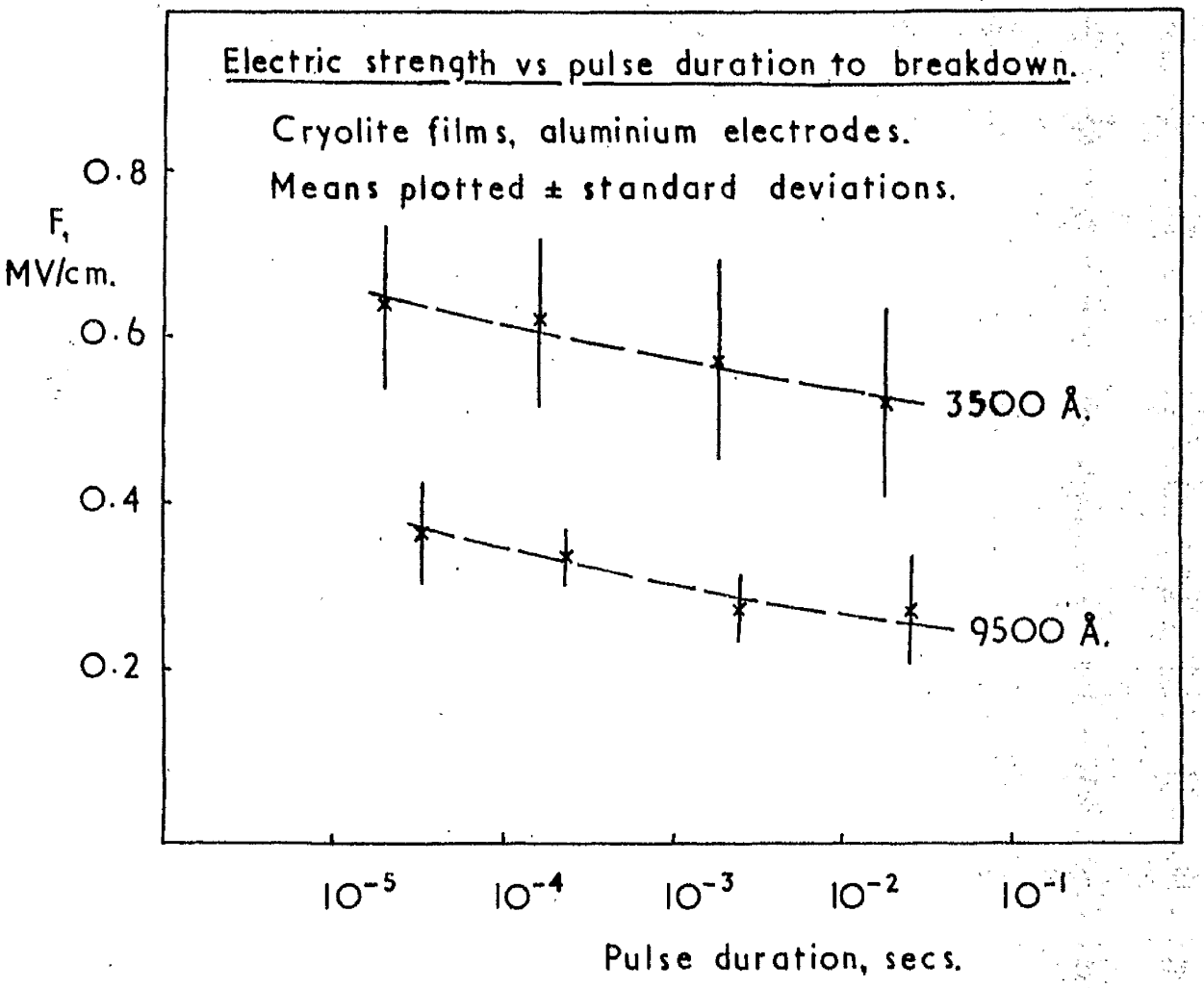

Electric strength vs pulse duration to breakdown.
Cryolite films, aluminium electrodes.
Means plotted ± standard deviations.
F, MV/cm.
0·8
0·6
0·4
0·2
3500 Å.
9500 Å.
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
Pulse duration, secs.

Fig.4.15

Table 4.1

Breakdown voltage results for cryolite films 3500 ± 500 Å thick tested at various rise rates.

Rise Rate $\frac{dV}{dt}$, V/msec	1040	132	10.6	1.4
$\log_{10} \frac{dV}{dt} \equiv x$	3.0170	2.1206	1.0253	0.1461
Breakdown voltage $\equiv y$	24	22	23	23
	26.5	24	24	23.5
	25	22	22	23.5
	25.5	25	22	22
	24	23	15	12
	17.5	16	15	12.5
	19	17	17	14
	25	17	20	15
	19	19	16	14.5
	18	19.5	17	17
		21	19	19.5
		18	23	18
		25	21	18
		24	21	19.5
		18	17	20.2
		21	20	20.8
		27	25	22.2
		22		21
		30		12
		28		15
				16
				23
				24
				20
Sample size	10	20	17	24

Table 4.2

Breakdown voltage results for cryolite films 9500 ± 500 Å thick tested at various rise rates.

Rise rate $\frac{dV}{dt}$, V/msec	1.4	10.6	132	1040
$\log_{10} \frac{dV}{dt} \equiv x$	0.1461	1.0253	2.1206	3.0170
Breakdown voltage $\equiv y$	42	28	33	45.5
	40	23	34.5	37
	20.5	27	27	26
	23	30	33.5	31
	29	20	34.5	29
	30	26	35.5	38
	20	35	31	36.5
	20	25	28	30.5
	27	28	38.5	44
	24	25.5	33	27
	31	26	31	34.5
	28	23.5	32	34
	26	24	37	36
	24.5	31	28.5	35
	25.5	31.5	26	29
	20		33	36
	26		39	42
	22		32	38
	30.5		26	36
			28	30
			31	28.5
			32	38
			30	35
Sample size	19	15	23	42

variation in V_B is small, any correlation between V_B and $\log \frac{dV}{dt}$ will also be approximately linear.

The observed values of V_B at the various values of rise rate are shown in Tables 4.1 and 4.2 for specimens of thickness 3500 ± 500 Å and 9500 ± 500 Å respectively.

Calculations. The correlation coefficient is defined as

$$r = \frac{\Sigma (x-\bar{x})(y-\bar{y})}{[\Sigma(x-\bar{x})^2 \Sigma(y-\bar{y})^2]^{1/2}},$$

where $\bar{x}$ and $\bar{y}$ are population means and where (here) $x \equiv V_B$ and $y \equiv \log_{10} (\frac{dV}{dt})$. In calculating the sums it is convenient to use the identities $\Sigma (x-\bar{x})^2 = \Sigma(x^2) - \frac{(\Sigma x)^2}{N}$, etc.

(a) Thickness = 3500 ± 500 Å (Table 4.1).

Population N = 71.

$$\Sigma x = (10 \times 3.0170) + (20 \times 2.1206) + (17 \times 1.0253) + (24 \times 0.1461) = \underline{93.518}$$

$$\Sigma y = 24 + 26.5 + \ldots + 20 = \underline{1445.2}$$

$$\Sigma x^2 = (10 \times 3.0170^2) + (20 \times 2.1206^2) + (17 \times 1.0253^2) + (24 \times 0.1461^2) = \underline{199.34}$$

$$\Sigma y^2 = 24^2 + 26.5^2 + \ldots + 20^2 = \underline{30502}$$

$$\Sigma xy = (24 + \ldots + 13) \times 3.0170 + (22 + \ldots + 28) \times 2.1206 + (23 + \ldots + 25) \times 1.0253 + (23 + \ldots + 20) \times 0.1461 = \underline{2014.9}$$

$$\Sigma(x - \bar{x})^2 = \Sigma(x^2) - \frac{(\Sigma x)^2}{N} = 199.34 - \frac{(93.518)^2}{71} = \underline{76.16}$$

$$\Sigma(y - \bar{y})^2 = \Sigma(y^2) - \frac{(\Sigma y)^2}{N} = 30502 - \frac{(1445.2)^2}{71} = \underline{1085}$$

$$\Sigma(x - \bar{x})(y - \bar{y}) = \Sigma(xy) - \frac{(\Sigma x)(\Sigma y)}{N} = 2014.9 - \frac{(1445.2)(93.518)}{71} = \underline{111.35}$$

$$\therefore r = \frac{\Sigma(x-\bar{x})(y-\bar{y})}{[\Sigma(x-\bar{x})^2\Sigma(y-\bar{y})^2]^{1/2}} = \frac{111.35}{[(1085)(76.16)]^{1/2}} = \underline{0.387}$$

"t" test

$$t = r\sqrt{\frac{N-2}{1-r^2}} = 0.387\sqrt{\frac{69}{1-0.387^2}} = \underline{3.49}$$

From tables (Fisher and Yates 1957, Table III),

At N - 2 = 60, probability that t > 3.460 is 0.001

At N - 2 = 120, probability that t > 3.373 is 0.001

Comparing these figures with the above results shows that the probability that the observed variation is due to the same causes as the scatter is about 0.001.

(b) Thickness = 9500 ± 500 Å (Table 4.2)

Population N = 99.

$\Sigma x = (19 \times 0.1461) + (15 \times 1.0253) + (23 \times 2.1206) + (42 \times 3.0170)$

$= \underline{193.64}$

$\Sigma y = 42 + 40 + \ldots + 28.5 = \underline{3108.5}$

$\Sigma x^2 = (19 \times 0.1461^2) + (15 \times 1.0253^2) + (23 \times 2.1206^2) +$

$+ (42 \times 3.0170^2) = \underline{501.90}$

$\Sigma y^2 = 42^2 + 40^2 + \ldots + 28.5^2 = \underline{101411}$

$\Sigma xy = (42 + \ldots + 30.5) \times 0.1461 + (28 + \ldots + 31.5) \times 1.0253 +$

$+ (33 + \ldots + 30) \times 2.1206 + (45.5 + \ldots + 28.5) \times$

$\times 3.0170 = \underline{6455.4}$

$$\Sigma(x-\bar{x})^2 = \Sigma x^2 - \frac{(\Sigma x)^2}{N} = 501.90 - \frac{(193.64)^2}{99} = \underline{123.15}$$

$$\Sigma(y-\bar{y})^2 = \Sigma y^2 - \frac{(\Sigma y)^2}{N} = 101411 - \frac{(3108.5)^2}{99} = \underline{3807.5}$$

$$\Sigma(x-\bar{x})(y-\bar{y}) = \Sigma xy - \frac{(\Sigma x)(\Sigma y)}{N} = 6455.4 - \frac{(193.64)(3108.5)}{99} = \underline{375.30}$$

$$\therefore \quad r = \frac{\Sigma(x-\bar{x})(y-\bar{y})}{[\Sigma(x-\bar{x})^2\Sigma(y-\bar{y})^2]^{1/2}} = \frac{375{\cdot}30}{[(123{\cdot}15)(3807{\cdot}5)]^{1/2}} = \underline{0{\cdot}548}$$

"t" test

$$t = r\sqrt{\frac{N-2}{1-r^2}} = 0{\cdot}548\sqrt{\frac{97}{1-0{\cdot}548^2}} = \underline{6{\cdot}45}$$

By comparing this result with the values already quoted from Fisher and Yates it can be seen that in this case the probability that the observed variation is due to random causes is well below 0.001.

CHAPTER 5

DIELECTRIC TESTS ON THIN FILMS EXPOSED TO MOISTURE.

5.1 Preliminary Work

To expose a specimen to moisture without exposing it to air at the same time it would be necessary to admit air-free water vapour to a vacuum enclosure initially at less than 10^{-4} torr. To achieve this would involve some experimental difficulty which would be unnecessary if it could be shown that dry air has no effect on the properties it is desired to study.

To verify in the first instance that moisture does effect the electric breakdown of evaporated dielectric specimens, some slides were coated with lithium fluoride films between aluminium electrodes and the films tested in atmospheric air after being exposed to it for about one hour. The results exhibited wider scatter and a somewhat higher mean value than the corresponding results for dry specimens (Fig.5.1).

To determine whether the increase was due to effects of the air or of the atmospheric moisture, some lithium fluordie specimens were tested in dry air admitted to the vacuum chamber after depositing the films by connecting a flask of fresh phosphorus pentoxide, open to the atmosphere, to the slow leak valve of the pumping unit. The results, plotted in Fig.5.2, lie within the scatter limits for the freshly deposited specimens tested in vacuum. Dry air therefore seems to have no detectable effect on the breakdown voltages measured. It follows that in studying the effect of water vapour on the electric breakdown

of/

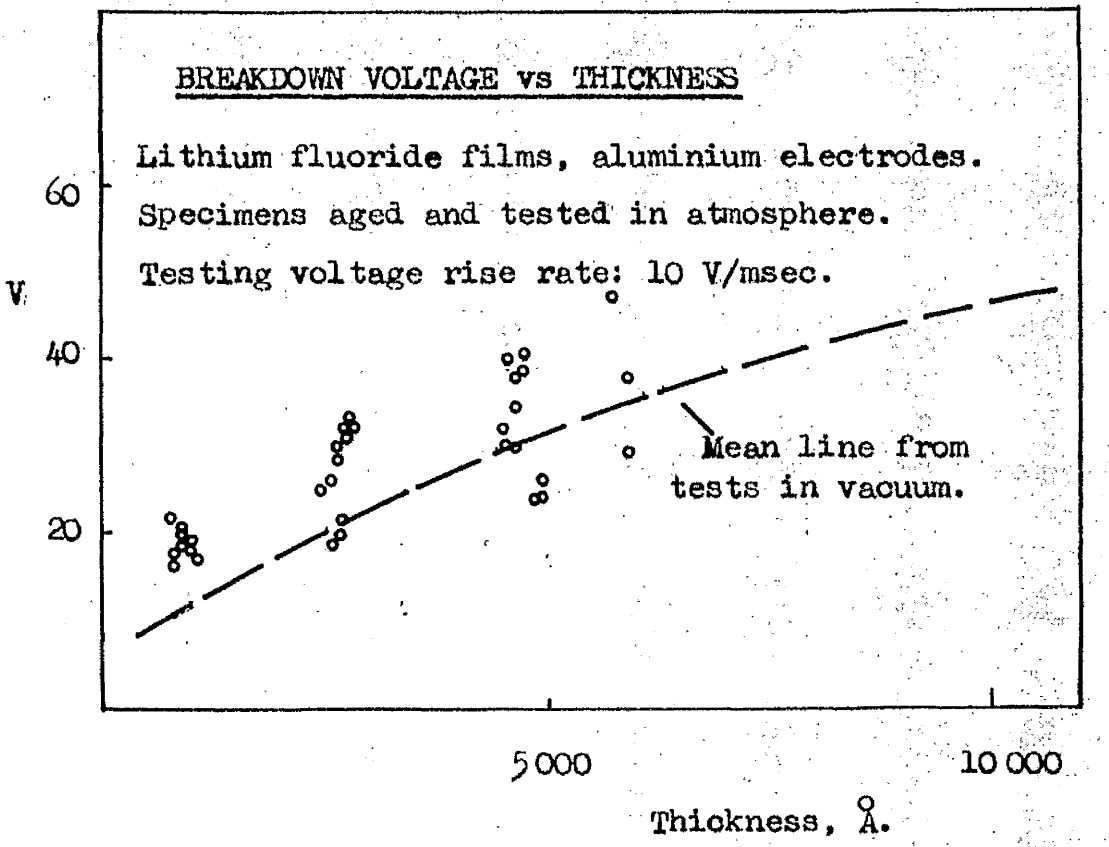

BREAKDOWN VOLTAGE vs THICKNESS
Lithium fluoride films, aluminium electrodes.
Specimens aged and tested in atmosphere.
Testing voltage rise rate: 10 V/msec.
V
60
40
20
Mean line from tests in vacuum.
5000
10 000
Thickness, Å.

Fig. 5.1

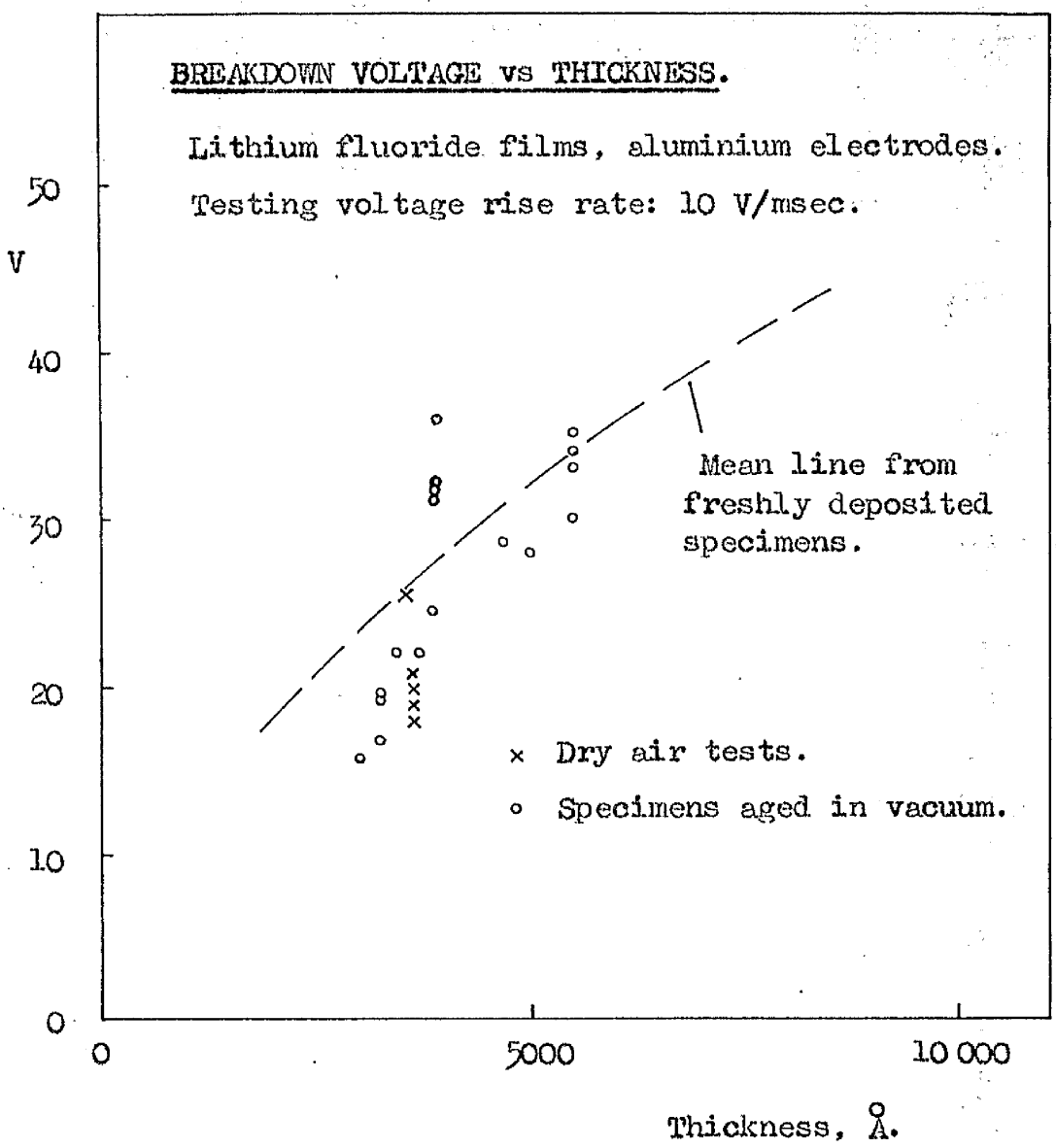

BREAKDOWN VOLTAGE vs THICKNESS.
Lithium fluoride films, aluminium electrodes.
Testing voltage rise rate: 10 V/msec.
V
50
40
30
20
10
0
0
5000
10 000
Thickness, Å.
Mean line from freshly deposited specimens.
× Dry air tests.
o Specimens aged in vacuum.

Fig.5.2

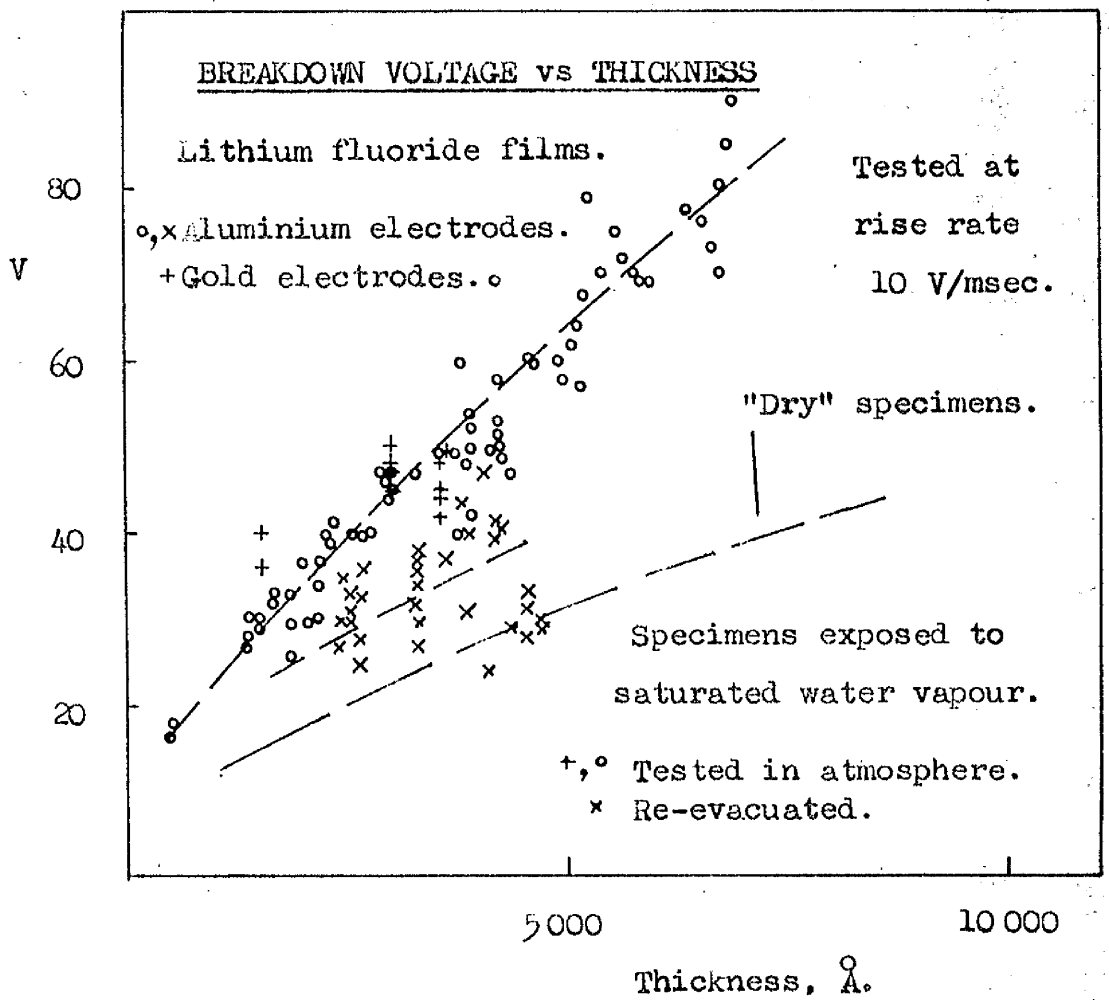

BREAKDOWN VOLTAGE vs THICKNESS
Lithium fluoride films.
o,x Aluminium electrodes.
+ Gold electrodes.
Tested at rise rate 10 V/msec.
"Dry" specimens.
Specimens exposed to saturated water vapour.
+,o Tested in atmosphere.
x Re-evacuated.
V
80
60
40
20
5000
10 000
Thickness, Å.

Fig. 5.3

of these specimens the moisture may be admitted in the presence of air at atmospheric pressure. The experimental difficulties are thus greatly reduced: a slide can be exposed to water vapour simply by placing it in a small enclosure above water at room temperature. In practice the slide was then replaced in the turntable and tested with the same apparatus as previously used.

5.2 Results for Lithium Fluoride Films Exposed to Moisture.

A graph of breakdown voltage against thickness for lithium fluoride films with aluminium electrodes is given in Fig.5.3. The specimens were aged over water and then tested in air at atmospheric pressure. Before testing, a vessel of water was laid on the baseplate of the vacuum system and the bell jar placed in position, so that the actual test took place in moist air.

The results are similar to those for dry specimens except in magnitude. At a given thickness the breakdown voltage is about twice as great as that of a freshly deposited film tested in vacuum. The results did not depend on whether the aging time was 5 minutes or one hour, which indicates that 5 minutes is sufficient time for a specimen to adsorb moisture virtually to saturation. An aging time of 5 minutes was therefore adopted as standard.

It was desirable to keep the aging time as short as possible because/

because of the effect of moisture on the electrodes. The tendency of aluminium electrodes to diffuse away from the fired silver contacts and so cause open circuits was reported in Section 4.2. The process seemed to be accelerated by the application of a field or by the presence of moisture, and failure of tests through open-circuiting was extremely frequent in specimens tested in moist conditions after being aged under such conditions for more than about an hour. Since these long aging times are not of particular relevance here, it was not considered necessary to go to the expense of using gold electrodes to study them.

The display on the oscilloscope screen during these tests was characteristic. At first the applied pulse was cut off at a low voltage, indicating short-circuiting of the generator output by a low resistance. By connecting various resistors across the generator output, the value of this resistance was estimated at about 100 Ω. On applying further pulses, the cut-off voltage began to rise, showing that the resistance was increasing, until breakdown pulses began to appear and the display changed its shape until it finally assumed the same form as in the tests on freshly deposited specimens in vacuum (Fig.4.3b).

Similar phenomena occurred when the testing voltage was increased manually. If the potentiometer was adjusted to a suitable setting and then left, the oscilloscope revealed that the/

the voltage across the specimen increased with time at an increasing rate until the breakdown voltage was reached. The values of breakdown voltage measured for lithium fluoride films with aluminium electrodes when the testing voltage was applied manually in this way are plotted in Fig.5.4. The results lie slightly below those obtained with pulses of faster rise rate, just as in the case of the specimens not exposed to moisture. For reference all four mean lines are included in the graph.

These observations suggest that we are dealing here with some such phenomenon as evaporation of excess free moisture from the films by Joule heating, or dielectric polarisation currents due to transport of dissolved ions in the moisture.

It is surprising that the change in breakdown field when moisture is present is an increase. Before considering possible effects of the moisture on the dielectric film it is necessary to know that the change in measured breakdown field is not due to effects of moisture on the aluminium electrodes. Six slides were therefore coated with lithium fluoride films between gold electrodes. Successful results were obtained from the tests in atmosphere on three of these specimens after exposure to moisture, and are included in Fig.5.3. They can be seen to lie within the scatter limits of the results taken with aluminium electrodes.

Since gold electrodes are unlikely to have been affected by moisture it can be concluded that the increase in breakdown/

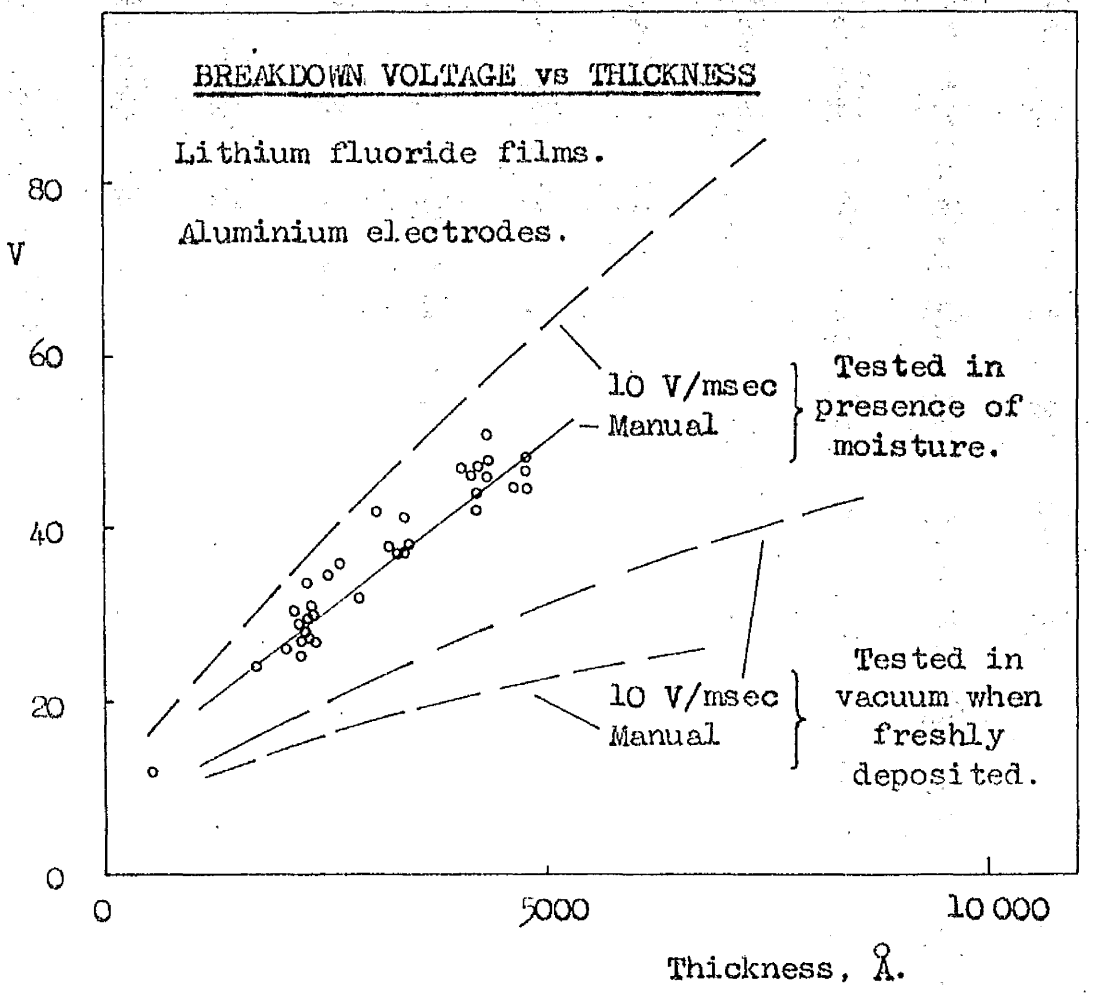

BREAKDOWN VOLTAGE vs THICKNESS
Lithium fluoride films.
Aluminium electrodes.
V
80
60
40
20
0
10 V/msec
Manual
Tested in presence of moisture.
10 V/msec
Manual
Tested in vacuum when freshly deposited.
0
5000
10 000
Thickness, Å.

Fig.5.4

field is due to processes occurring within the dielectric film itself. Two possible explanations suggest themselves. Firstly, after excess moisture has been removed by heating, some more strongly bound water may remain in the form of adsorbed layers on the dielectric film and possibly affect electronic processes. Alternatively, the recrystallisation which is known to take place when a lithium fluoride film is exposed to moisture (Mullen 1964 - see Sub-section 1.2.3) may affect its breakdown field.

A method of attempting to distinguish between these possibilities was suggested by the dielectric constant and loss tangent measurements of Weaver (1962), who found large changes in ε' and $\tan\delta$ when moisture was admitted to a film. In relatively insoluble dielectrics such as lithium fluoride, however, these effects were completely reversible, ε' and $\tan\delta$ returning to their original values when the specimens were dried by keeping them in vacuum for a few minutes, even at a pressure as high as 10^{-2} torr. One would therefore expect that all residual moisture could be removed from a dielectric film by keeping it in vacuum. If the increase in breakdown field were due to residual water, the breakdown field would then be expected to return to the same value as in a freshly deposited film of the same thickness. If however the increase were due to recrystallisation, one would expect the high value of breakdown field to be maintained.

Lithium/

Lithium fluoride specimens with aluminium electrodes were tested in vacuum after being exposed to water vapour for 5 minutes and then pumped down and maintained at about 10^{-4} torr for about an hour. The results are included in Fig.5.3. Their mean values lie below those obtained with the specimens tested in moist air, but are still above the results for freshly deposited specimens. The display on the oscilloscope screen had now lost the initial 'short-circuited' appearance associated with the atmospheric tests and reverted to a shape similar to the one seen in testing freshly deposited specimens in vacuum (Fig.4. 3b). This fact confirms the interpretation of the displays that occurred in the atmospheric tests as corresponding to a driving off of excess free moisture from the dielectric film.

It seems unlikely that these results have been in any way affected by aging of the film. It has already been pointed out that the value of the breakdown field after aging for periods of about an hour in the presence of moisture is not measurably different from its value after exposure to water vapour for only 5 minutes. The total time which elapsed between exposing a film to moisture and finally testing it after keeping it in vacuum was about 1½ hours, and any tendency to aging in a period of this order would have been noticeable after an hour. On the other hand from Weaver's observations it seems likely that the specimens kept in vacuum would be practically free of moisture for most of the/

1½ hour period, and it is just possible that aging could occur under dry conditions but not in the presence of moisture. However the results of a series of tests on lithium fluoride films aged in vacuum for about 12 hours without having been exposed to moisture (included in Fig.5.2) lie within the scatter limits for freshly deposited specimens and thus show no aging effect for periods of this order.

Since the breakdown fields of the specimens that were exposed to moisture and then kept in vacuum have not returned to their original value, the results tend to suggest that recrystallisation rather than adsorbed moisture is responsible for the increased breakdown fields. The fact that the final value of breakdown field depends on whether moisture is removed by re-evacuation or by applying pulses may be due to an effect, in the latter case, of Joule heating or of the presence of the field on the way in which the new structure forms. On the other hand an interpretation in terms of adsorbed moisture is still possible, because there may have remained on the films tested after re-evacuation an amount of water too small to affect ε' and $\tan\delta$ but sufficient to affect breakdown processes. A third possibility is that recrystallisation tends to increase the breakdown field to the value observed after re-evacuation, but that adsorbed moisture also has an effect and that in the tests performed in moist air the two effects have been superimposed.

In/

In the atmospheric tests moisture may have been only partly removed and the recrystallisation process may have been modified by applying the pulses. In the tests performed after re-evacuation moisture must have been almost completely removed and no effect on the recrystallisation process can have been possible. Some means of separating the effects of moisture and of the field was necessary. This was achieved as follows. Lithium fluoride specimens with aluminium electrodes were first exposed to saturated water vapour for 5 minutes. The slides were then replaced in the vacuum chamber and pulses were applied to each specimen in turn until enough moisture had been driven off for the breakdown voltage to be reached. The chamber was then evacuated and kept at less than 10^{-4} torr for an hour. The specimens were then tested in the usual way with 10 V/msec pulses. Thus although almost all moisture had been removed, the specimens had been exposed to a field almost equal to the breakdown field, and to Joule heating, at the time when any effects on the recrystallisation process would have been taking place.

The results are plotted in Fig.5.5 together with the mean lines of all previous sets for lithium fluoride tested at 10 V/msec. The new results have a higher mean value than any of the other sets and also show wider scatter, the breakdown fields of some specimens reaching values such as might be expected on the basis of the published breakdown fields of single crystals. It is not possible to/

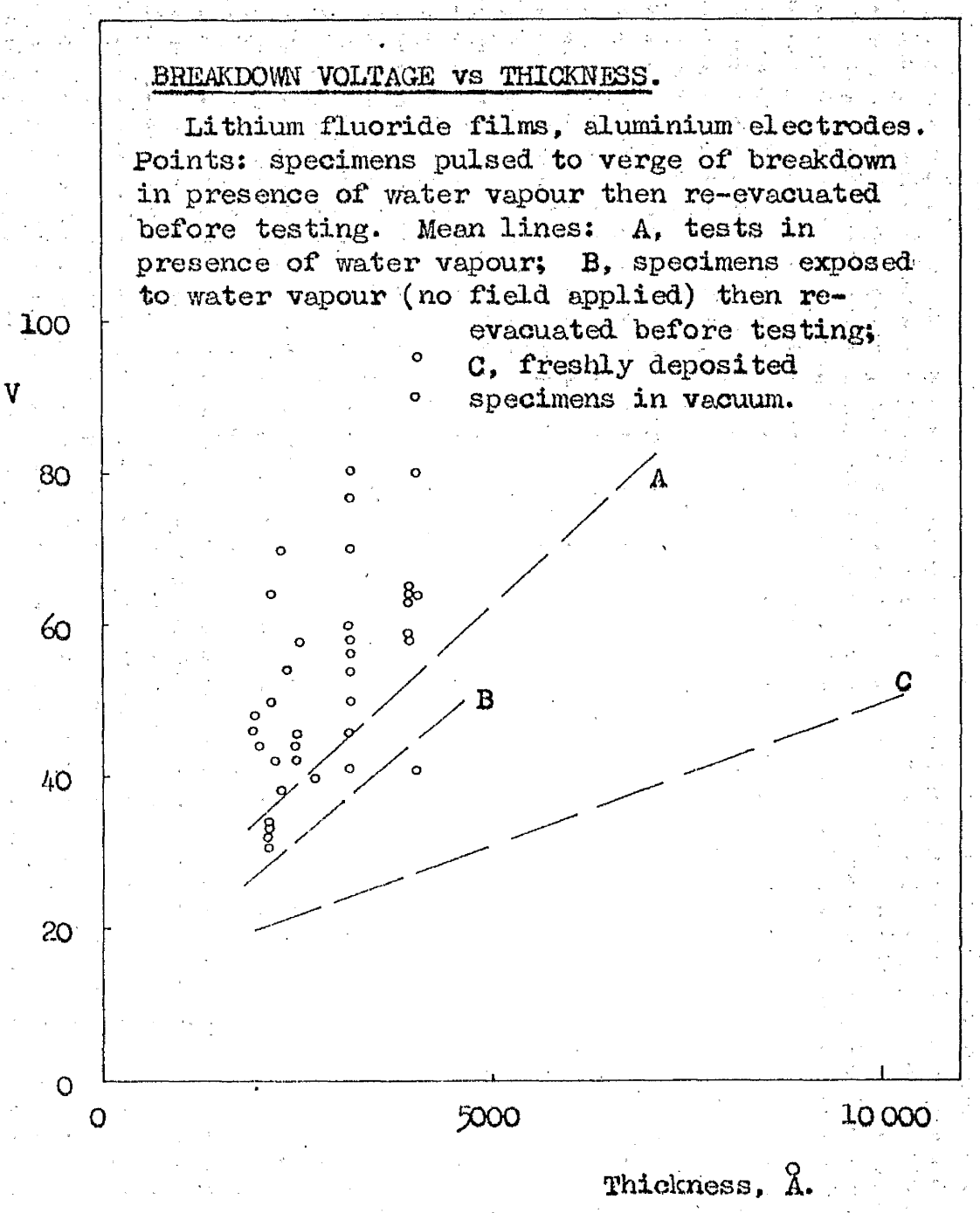

BREAKDOWN VOLTAGE vs THICKNESS.
Lithium fluoride films, aluminium electrodes. Points: specimens pulsed to verge of breakdown in presence of water vapour then re-evacuated before testing. Mean lines: A, tests in presence of water vapour; B, specimens exposed to water vapour (no field applied) then re-evacuated before testing; C, freshly deposited specimens in vacuum.
V
100
80
60
40
20
0
A
B
C
0
5000
10 000
Thickness, Å.

Fig. 5.5

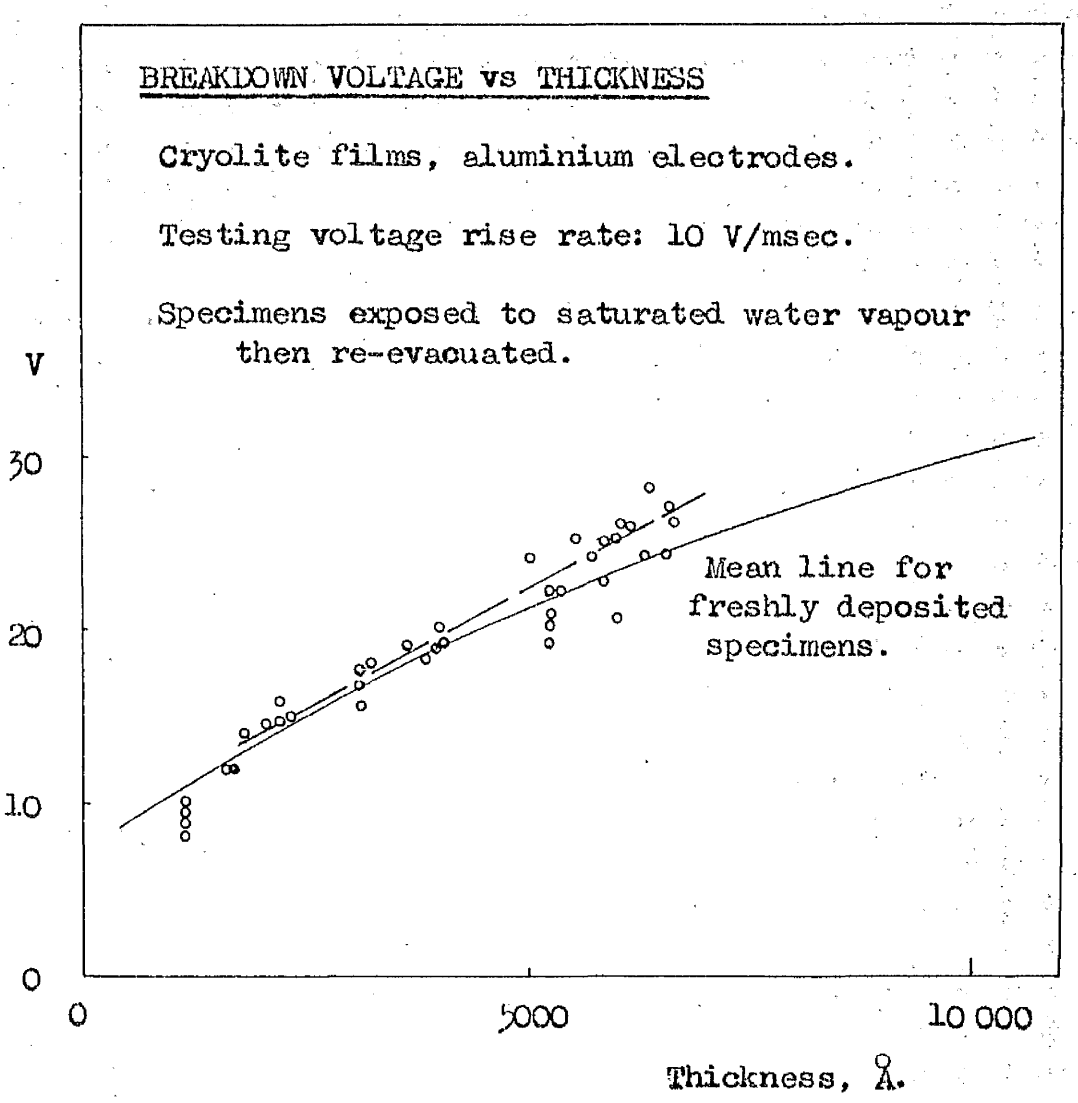

BREAKDOWN VOLTAGE vs THICKNESS
Cryolite films, aluminium electrodes.
Testing voltage rise rate: 10 V/msec.
Specimens exposed to saturated water vapour then re-evacuated.
V
30
20
10
0
0
5000
10 000
Thickness, Å.
Mean line for freshly deposited specimens.

Fig. 5.6

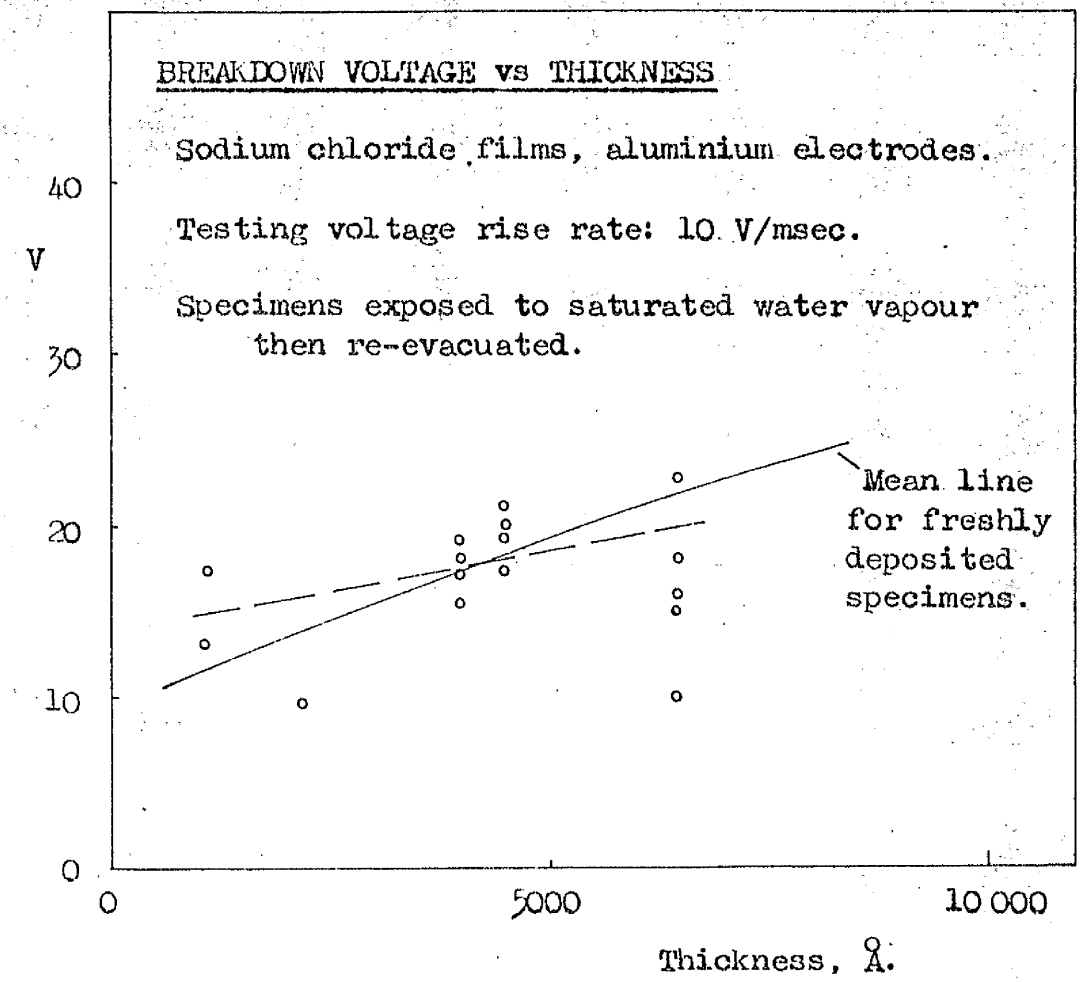

BREAKDOWN VOLTAGE vs THICKNESS
Sodium chloride films, aluminium electrodes.
Testing voltage rise rate: 10 V/msec.
Specimens exposed to saturated water vapour then re-evacuated.
V
40
30
20
10
0
0
5000
10 000
Thickness, Å.
Mean line for freshly deposited specimens.

Fig. 5.7

to offer an explanation of why the breakdown field should increase in this way. However of the three interpretations suggested above for the behaviour of the breakdown field when moisture is admitted, this last observation strongly suggests the one in terms of recrystallisation which may be influenced by Joule heating or by the presence of an electric field.

5.3 Results for Cryolite and Sodium Chloride Films Exposed to Moisture.

Only in lithium fluoride have the effects of moisture been fully investigated, but some measurements were made with cryolite and sodium chloride films with the object of finding whether moisture has a similar effect. In the case of cryolite the results plotted in Fig.5.6, which are for specimens exposed to saturated water vapour at room temperature for 5 minutes and tested after re-evacuation, seem to indicate a slight effect, but the increase is much smaller than in lithium fluoride.

In sodium chloride it was difficult to obtain any results at all. This is not surprising in view of the known tendency for soluble films to disintegrate completely when exposed to moisture (Sub-section 1.2.5). Although a few results were obtained after re-evacuation when the time of exposure of the film to the water vapour was reduced to 1 minute (Fig.5.7), they do not permit a conclusion to be drawn as to whether the breakdown field increases in this material also when moisture is admitted.

CHAPTER 6

DISCUSSION.

6.1 The Magnitude of the Breakdown Field.

Published experimental evidence on alkali halides in bulk form suggests an avalanche type of breakdown mechanism (Sub-section 1.3.5). For sodium chloride a theoretical curve given by Stratton (1961) on the basis of the single-electron avalanche breakdown theory predicts an electric strength of about 2 MV/cm at 10 000 Å. At this thickness the present results give a value of 0.2 MV/cm. The theoretical curve predicts values perhaps slightly higher than the lowest experimental results of previous workers (see Section 1.6), but the present results seem lower by a factor of nearly 10 than the earlier values would lead one to expect.

In Section 1.6 it was suggested that the most reliable value for the breakdown field of sodium chloride specimens of thickness of the order of tenths of a millimetre was 0.75 MV/cm. The corresponding value for lithium fluoride was estimated at roughly 1.5 MV/cm. In the present investigation the breakdown field of a lithium fluoride film 10 000 Å thick was measured as about 0.5 MV/cm. These figures suggest that the present results are again lower than one would expect by a factor of about 10. No measurements of the electric strength of cryolite have been seen in the literature, but the present results seem unduly low in this material also.

In attempting to account for the low values two main possibilities/

possibilities must be borne in mind: (i.) breakdown has not been intrinsic; (ii.) breakdown has been intrinsic but complicating effects have led to low electric strengths. In the following sections possible explanations under both these headings are considered.

6.2 Ambient Medium Discharges.

The general design of the apparatus, and the magnitude of the voltages used, would not lead one to expect any complications due to gas discharges, but the question must be discussed in more detail.

Under stated conditions, and at a particular specimen thickness, discharges will occur when the breakdown voltage of the surrounding gas is less than that of the solid specimen. In the present investigation, the condition that would be expected to give the lowest gas breakdown voltage, namely an environment of moist air, is also the condition that gives the highest measured breakdown voltages. It follows that the lower breakdown voltages, those measured in dry air or in vacuum, cannot have been affected by extraneous discharges. The fact that the tests in dry air gave similar results to those performed in vacuum, and the fact that the highest voltages involved (about 50 volts in dry specimens) are well below the minimum in the Paschen curve for air (300 volts), tend to confirm this conclusion.

Hence the only results that may have been affected are those for/

for specimens tested in moist air. Even here, however, the possibility is a remote one. The specimens seem to have been largely dried out before breakdown took place because of heating by conduction currents, and hence the surroundings would not in general have been saturated with water vapour. The minimum breakdown voltages of the surroundings would therefore not be much below the minimum in the Paschen curve for dry air. So here again the voltages involved are too low. They are certainly too low in the thinner specimens, and there are no discontinuities in the breakdown voltage-thickness curve (Fig.5.3) such as one might expect if a transition to a different mechanism occurred at some intermediate thickness. The curve is in fact of a similar shape to the curve for dry specimens.

Thus one may safely conclude that ambient medium discharges have not affected any of the results, and it is quite certain that they have not affected the results obtained by testing in vacuum or in dry air.

6.3. Chemical Effects

In lithium fluoride and sodium chloride the possibility of chemical changes during deposition is negligible, and the breakdown field cannot have been affected in this way either in its magnitude or in its dependence on specimen thickness or pulse duration.

In cryolite, Koppelmann et al. (1961) suggested on the basis of refractive index measurements that some of the material decomposed while being deposited. Because of the uncertainty as to the refractive/

index of bulk cryolite their suggestion cannot be taken as established (see Sub-section 1.2.4). Nevertheless the possibility of partial decomposition must be considered.

Firstly, the magnitudes of the breakdown fields may have been affected. Since however no previous values of the electric strength of cryolite are available for comparison, this possibility is not relevant to the interpretation of the present results.

The question of possible effects on the dependence of breakdown field on applied voltage duration, on the other hand, is of some importance since this dependence was studied in detail only for cryolite. However in lithium fluoride and sodium chloride the breakdown fields measured with a voltage increased manually at about 0.01 V/msec were lower than those measured with a voltage increased electronically at about 10 V/msec (Figs.4.12 and 4.13). Moreover the three dielectrics behaved similarly in all other respects in which they were directly compared. These facts suggest that the decrease in the breakdown field of cryolite with increasing pulse duration is unlikely to be due to decomposition and that the breakdown fields of lithium fluoride and sodium chloride would exhibit a similar dependence.

Chemical changes on aging, like other aging effects, are excluded for the reasons given in Section 4.2. In any case chemical aging is most unlikely in these simple inorganic materials, and is out of the question in the specimens tested immediately after deposition./

6.4 Thermal Breakdown.

In the simple general theory of thermal breakdown (see Whitehead 1951), the rate $\frac{dT}{dt}$ at which the temperature of a volume element of the dielectric increases is equated to the sum of the rate of heat generation in the element and the rate at which heat enters the element. This leads to the equation

$$\rho c \frac{dT}{dt} = \text{div } k \text{ grad } T + \sigma F^2 \qquad (6.1)$$

where ρ is the density of the dielectric, c its specific heat, k its thermal conductivity, σ its electrical conductivity, and F the applied field.

Usually the function $\sigma(T,F)$ is known at least approximately. With a typical form of this function and typical boundary conditions, it can be shown that there exists a critical value F_B of F, below which a steady state is possible but above which the temperature T of the lattice increases indefinitely, reaching the critical temperature T' for disintegration of the lattice after a formative time lag which can be obtained by integrating equation (6.1).

A simplified equation given by Stratton (1961) is applicable to the particular case of a thin slab. The temperature throughout the slab may be taken as uniform but different from the ambient temperature T_a. The function div k grad T cannot then be used, but if the rates of heat loss per unit area from the two sides of the/

the slab are taken as H_1 and H_2, and if the thickness of the slab is δ, the equation may be rewritten

$$\delta \rho c \frac{dT}{dt} = \delta \sigma F^2 - (H_1 + H_2) S, \tag{6.2}$$

where S is the area of one face of the slab.

Integration of equation (6.2) is comparatively simple. One obtains for the formative time lag

$$t_f = \delta \rho c \int_{T_a}^{T'} \frac{dT}{\delta \sigma F^2 - (H_1 + H_2) S}. \tag{6.3}$$

In this equation, and also in the more general one, the rate of heat loss appears in the denominator of the integral. The rate of heat loss per unit volume will be higher in a thin specimen than in a bulk specimen. Hence a comparatively long time to breakdown is to be expected under identical conditions of overvoltage. Since time lags in thermal breakdown are of the order of seconds or longer (Whitehead 1951), one can expect at least this order of magnitude in thin film specimens. In the present results the total time interval from the start of the applied pulse to the occurrence of breakdown was as little as 20 microseconds at the highest pulse rise rates used. This interval is not the same as the formative time lag, for in deriving equation (6.3) t_f is defined on the assumption that the voltage leading to breakdown is applied instantaneously and then held constant. In the present work the applied voltage was increased at an approx-uniform rate from zero, and consequently less heat would/

be developed within a given time interval from the start of the pulse. Hence t_f must be much shorter than 20 microseconds. In thermal breakdown one would expect a time lag at least five orders longer than this value.

Another effect of a long time lag to breakdown would be to allow voltage overshoot above the breakdown value before breakdown could take place. Equation (6.3) shows that t_f decreases rapidly with increasing overvoltage, but with a time lag several orders longer than the applied pulse duration a large overshoot would still be possible at high rise rates. This effect would be detected as a strong dependence of the measured breakdown field on the pulse duration. In the present results, Fig.4.15 shows the variation to be only about 30% over three orders of magnitude.

Finally, there was normally no evidence of the large pre-breakdown current that would precede thermal breakdown. A current of this magnitude would be detected by a lowering below its open-circuit value, prior to breakdown, of the voltage displayed on the oscilloscope screen. The shape of the display for some of the cryolite specimens tested at low rise rates (Fig.4.14) suggests a transition to a different breakdown mechanism, for not only did the display indicate pre-breakdown current, but also the breakdown voltage in these tests was reduced and showed wider scatter than the results usually obtained.

The observations described in this section show that breakdown was not thermal except possibly in the cryolite specimens just /

just mentioned.

6.5 Contamination of the Substrate.

6.5.1 Contamination by large particles. Any dust particles, etc., accidentally left on the substrate surface in the earlier stages of the cleaning process could reduce the effective thickness of the dielectric film locally and could also give rise to local field concentrations. Both effects could cause weak spots in the dielectric. However only small numbers of those particles were seen on slides examined under the microscope (it was estimated that there were from 15 to 200 within the area of one sandwich), and if they had been responsible for the low values of breakdown field one would have expected the successive breakdowns of at least some of the sandwiches to take place at gradually increasing voltages. In fact the breakdown voltage remained approximately constant as indicated in Fig.3.3b, with no systematic increase except occasionally in the first few breakdowns. This suggests that dust particles will not affect the breakdown field finally measured.

Similar considerations suggest that the breakdown field will not be reduced by local flaws such as small chips in the glass surface.

6.5.2. Chemical contamination. The breath test (e.g. Holland 1956, p.73) was occasionally applied to slides after they had been cleaned in the glow discharge and a black breath figure was always obtained. However although this is often taken as evidence/

evidence for lack of contamination, Holland (1953) has shown that a black figure may be formed even on a contaminated slide if silicone oil is used in the diffusion pump as in the present investigation. Holland (1953) also states, on the other hand, that contamination films of this kind are visible since they absorb light. A slide was therefore exposed to the glow discharge for several hours, but even after this treatment no light-absorbing film could be seen. It is thus most unlikely that an appreciable contamination layer could be formed in the time (10 - 15 minutes) for which slides to be used as substrates were exposed to the glow discharge.

6.6 Edge Effects.

In spite of the precaution of evaporating electrodes with diffuse edges, it is possible that some edge effects have occurred. Gaseous discharges near the electrode edges have already been excluded along with other types of ambient medium discharge (Section 6.2), but the dielectrics themselves may have tended to break down preferentially near the edges. Information on this possibility was obtained by examining specimens with gold and aluminium electrodes and studying the distribution of the markings caused by removal of the metal on breakdown (this check could not be performed on specimens with silver electrodes since the spot at which breakdown had occurred was usually not visible). A concentration of markings near the edges in many specimens, particularly the thinner ones, revealed/

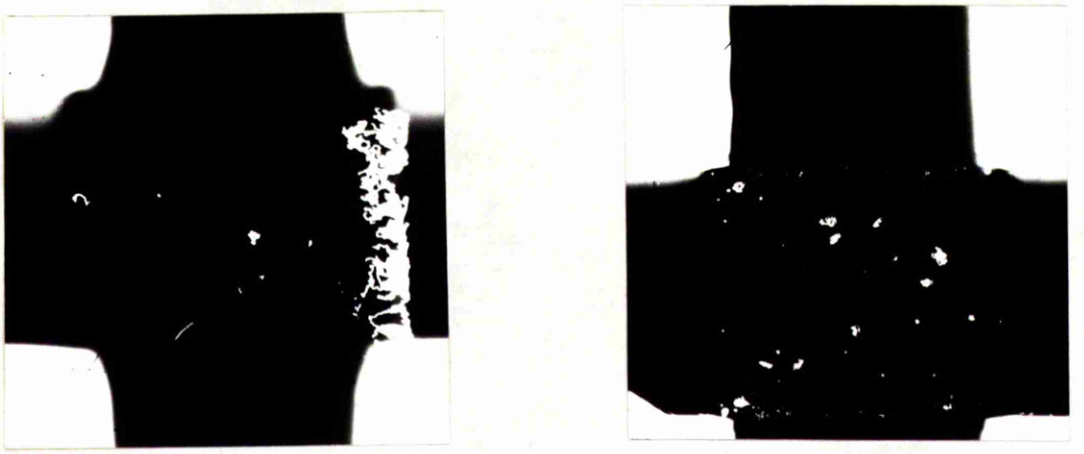
revealed a strong tendency for breakdown to occur there (see Plate 3a). Other specimens, however, showed a fairly uniform distribution over their whole area (Plate 3b). The breakdown fields lay within the same scatter limits no matter how the breakdown markings were distributed. This observation suggests that breakdown may tend to occur near the edges without appreciable reduction of the measured breakdown field. Possibly the applied field strength is increased near the electrode edges, but only slightly because of the diffuseness of the edges. In any case the order-of-magnitude discrepancy from previous results cannot be due to edge effects.

6.7 Effects of the Electrode Work Function.

It was shown in Section 4.2 that the measured breakdown fields have not been affected by the electrode work functions, either through internal fields or through effects of the potential barrier at the cathode surface. The low breakdown fields thus cannot be accounted for in this way.

In passing it may be noted that the fact that the breakdown fields with different cathode materials are not measurably different is in accordance with the observations of Cooper and Smith (1961) referred to in Sub-section 1.3.3.

It is at first sight surprising that internal fields have not affected the results obtained when the underlayer and the overlayer were not of the same metal. However assuming the values quoted/



(a) (b)

Plate 3

Specimens after breakdown x 10. (a) showing breakdown markings concentrated at electrode edge; (b) showing markings relatively uniformly distributed.

quoted in Section 4.2 for the work functions of silver, aluminium, and gold, and taking the three metals in pairs, the greatest difference in work function is about 0.75 eV between gold and aluminium. In spite of the disagreement between different authors as to the values of work function, this figure will be correct as regards order of magnitude. With these three metals, therefore, the differences in work function are much too small to be detected in the present work unless impracticably large numbers of specimens are tested.

6.8 Other Electrode Effects.

Low breakdown voltages could also be caused by penetration of overlayer metal into pinholes, etc., in the dielectric film during deposition. The effective thickness of the film would be reduced, and local field concentrations could arise. However Weaver (1962) found a low breakdown voltage even when the evaporated metal overlayers were replaced by foil electrodes pressed lightly on to the dielectric surface with a sponge rubber pad.

Further evidence is provided by the results of the present investigation. It is well known that metals differ in their ability to contour a surface accurately (Tolansky 1948). Hence, if penetration were seriously affecting the results, one would expect the measured breakdown voltage to depend on the overlayer metal when dissimilar metals were used. In fact it has been shown that the only detectable dependence on the electrode metal is a depression of the/

the result when the anode is of silver. This suggests that penetration of metal into pinholes is not of great importance. The fact that the breakdown voltages were actually smaller when the metal vapour from which the overlayer was condensed was obliquely incident tends to support this conclusion.

These observations do not exclude the effects of long-range variations in the dielectric thickness. If however breakdown were taking place at long-range thickness minima, one would expect successive breakdowns of a given specimen to take place at gradually increasing voltages. It was pointed out in Sub-section 6.5.1 that the breakdown voltage does not increase in this way, except occasionally at the start of the first pulse applied. This suggests that although a few penetrations of overlayer metal may have taken place the resulting weak spots would be burnt out at the start of the test.

Alternatively, it is possible that there exist in a film numerous thin spots of about the same thickness, so that repeated breakdowns take place at the same voltage until all the electrode has in effect been removed. One would not expect very large field concentrations to result from these long-range thickness variations, and therefore all the depression of the breakdown field would have to result from the actual change in film thickness. It was shown above that the results are lower than the published values by a factor of about 10. Hence if the entire discrepancy were to be accounted/

accounted for in this way there would have to exist a large number of spots at which the dielectric thickness was only about a tenth of the mean thickness as measured interferometrically. Electron micrographs given by Weaver (1962) and by Mullen (1964) suggest that this is most unlikely.

The conclusion seems to be that pinholes and other short-range thickness variations have not affected the breakdown voltages. Longer-range variations may have had some effect, but it is unlikely that they could account for the entire discrepancy from the published values.

Possible effects of field concentrations due to the structure of the metal films are referred to in Section 6.10.

6.9 The Breakdown Mechanism.

From the foregoing sections it seems that the low values of breakdown field are not due to extraneous effects or non-intrinsic breakdown. Direct confirmation of this conclusion is supplied by the fact that in some of the specimens exposed to moisture the breakdown fields approached the higher values expected on the basis of results for bulk materials (Section 5.2). The low values must therefore have a more fundamental cause, whose exact identification will require knowledge of the breakdown mechanism.

From the above discussion it seems that breakdown has been intrinsic, but it is desirable to know what type of intrinsic mechanism has been operative. The evidence at present available from previous studies/

studies suggests that the breakdown of bulk single crystals is of the avalanche type (see Sub-section 1.3.5). This suggests that the same is true in evaporated films, but it is not difficult to envisage how complications due to the structure of the films could affect the breakdown mechanism. More direct evidence on thin films is therefore required.

The results of Plessner (1948) in general show that the breakdown field in thin films increases with decreasing thickness. This behaviour is qualitatively in accordance with the theory of avalanche breakdown. The present results also show an increase in breakdown field with decreasing thickness. This can be seen from Figs.6.1 to 6.3, where the results in Figs.4.8, 4.10 and 4.11 for cryolite, lithium fluoride, and sodium chloride films respectively with aluminium electrodes are replotted as graphs of breakdown field against thickness. The fact that the dependence extends up to thicknesses of the order of 10 000 Å suggests that one of the later avalanche theories applies rather than Frohlich's early theory which predicts a dependence only when the thickness decreases to approach the electron mean free path (cf. Section 2.2).

However the thickness dependence must be viewed with caution as evidence for avalanche breakdown, because the mechanism causing the breakdown field to be small in magnitude may also affect its thickness dependence. If the results could be shown to be a good fit to some theoretical relation then the evidence for avalanche breakdown would be stronger. Two theoretical equations for the dependence/

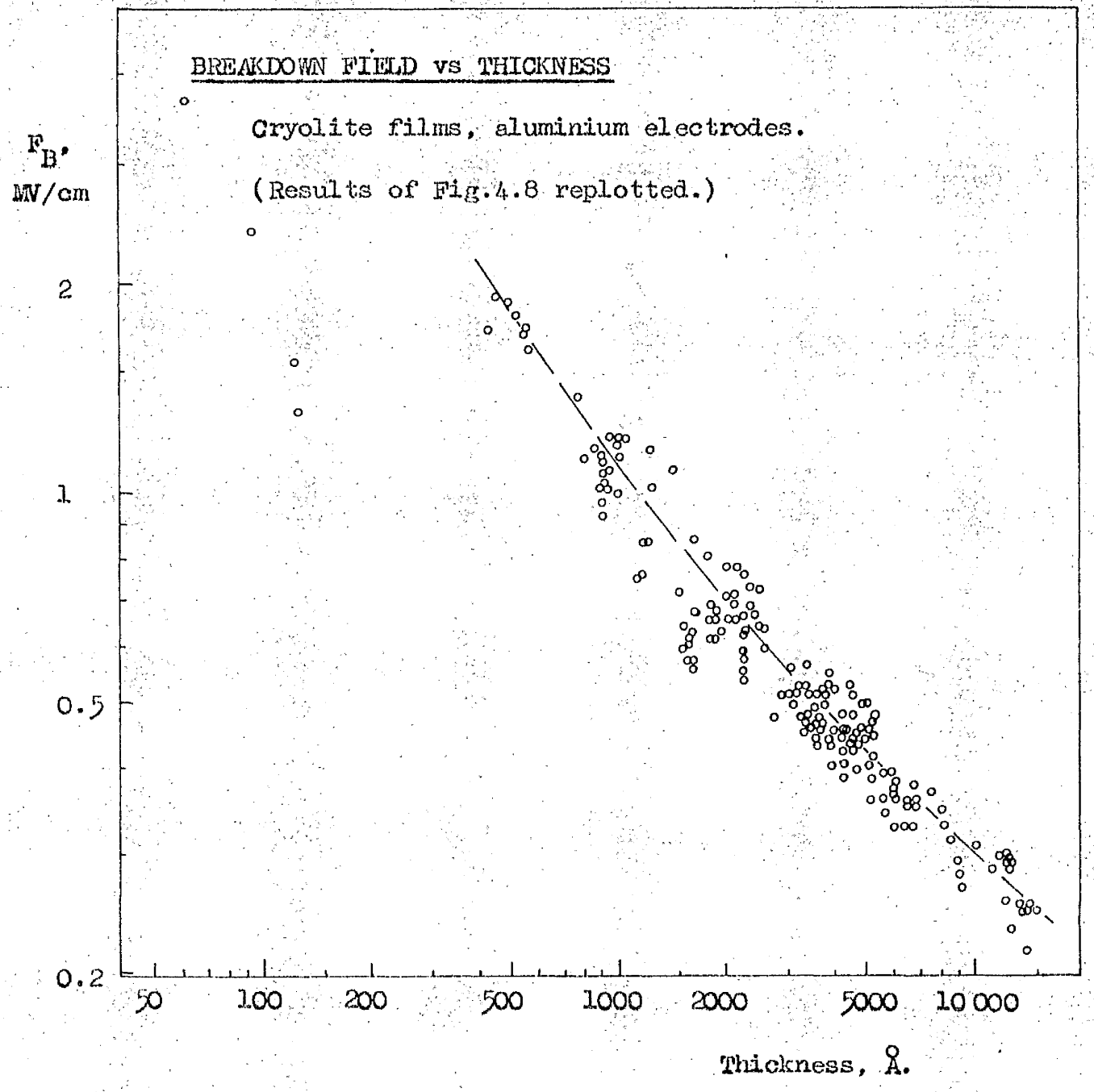

BREAKDOWN FIELD vs THICKNESS
Cryolite films, aluminium electrodes.
(Results of Fig.4.8 replotted.)
F_B, MV/cm
2
1
0.5
0.2
50
100
200
500
1000
2000
5000
10 000
Thickness, Å.

Fig.6.1

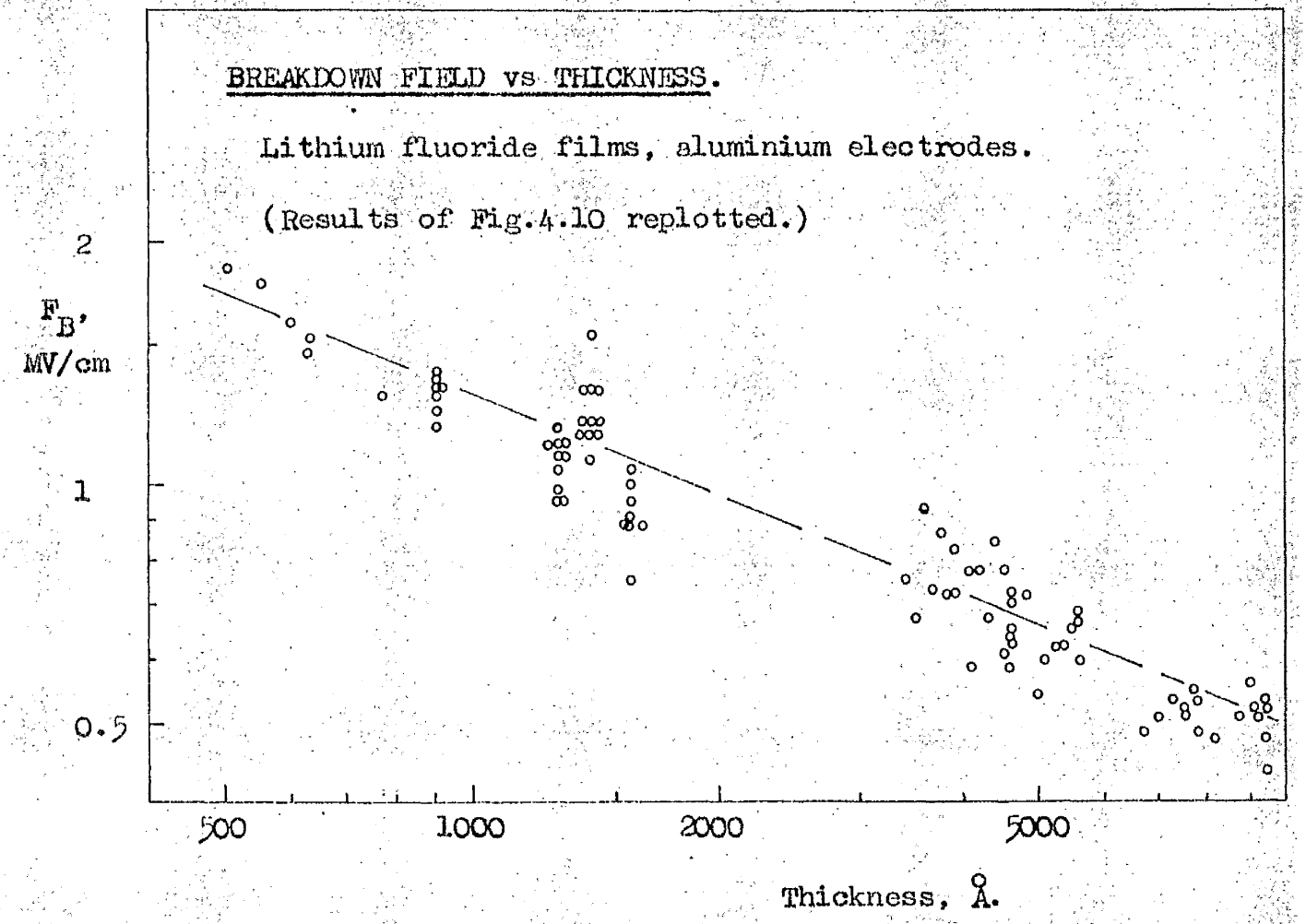

BREAKDOWN FIELD vs THICKNESS.
Lithium fluoride films, aluminium electrodes.
(Results of Fig.4.10 replotted.)
2
F_B, MV/cm
1
0.5
500
1000
2000
5000
Thickness, Å.

Fig.6.2

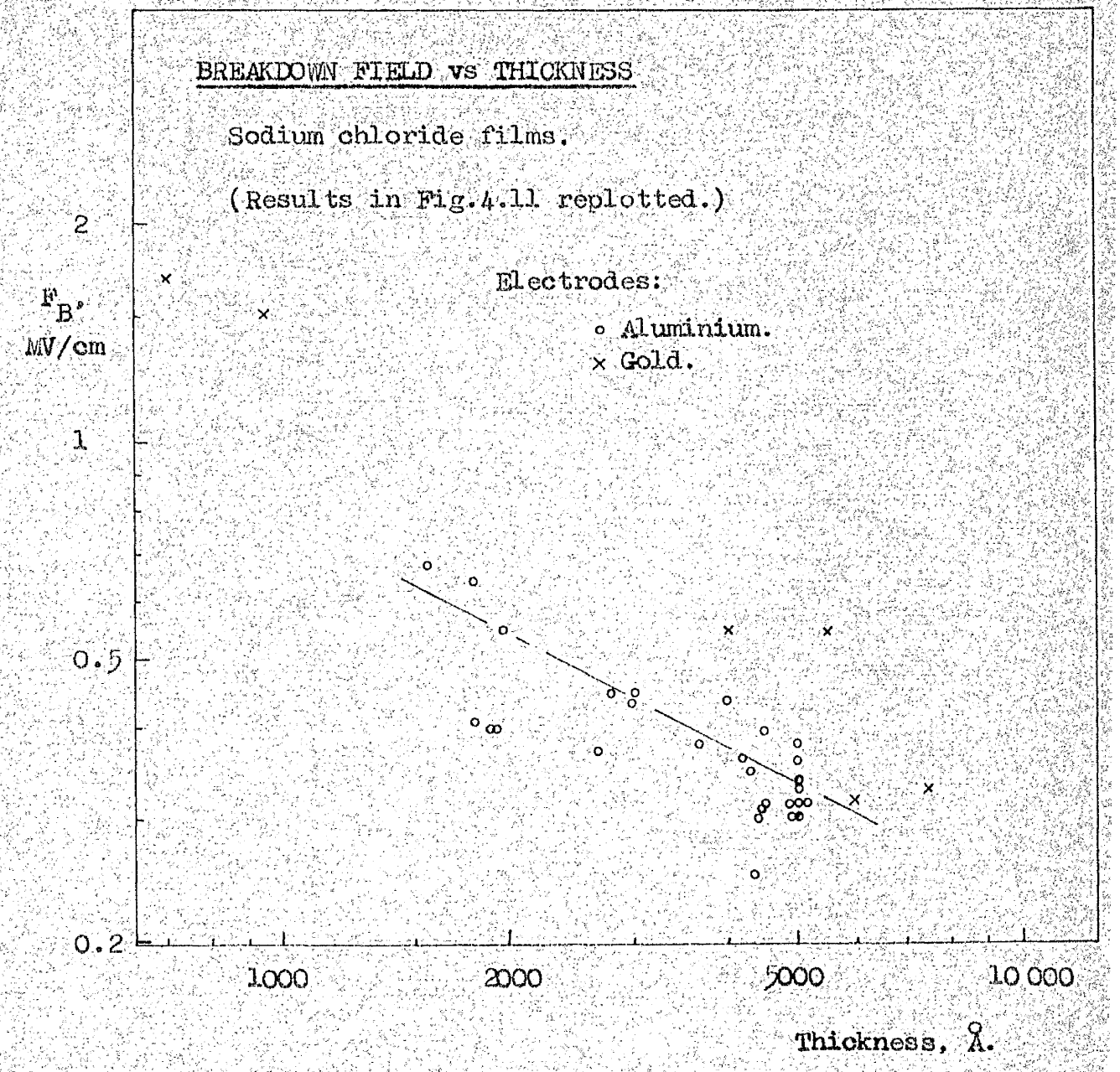

BREAKDOWN FIELD vs THICKNESS
Sodium chloride films.
(Results in Fig.4.11 replotted.)
Electrodes:
o Aluminium.
× Gold.
F_B, MV/cm
2
1
0.5
0.2
1000
2000
5000
10 000
Thickness, Å.

Fig.6.3

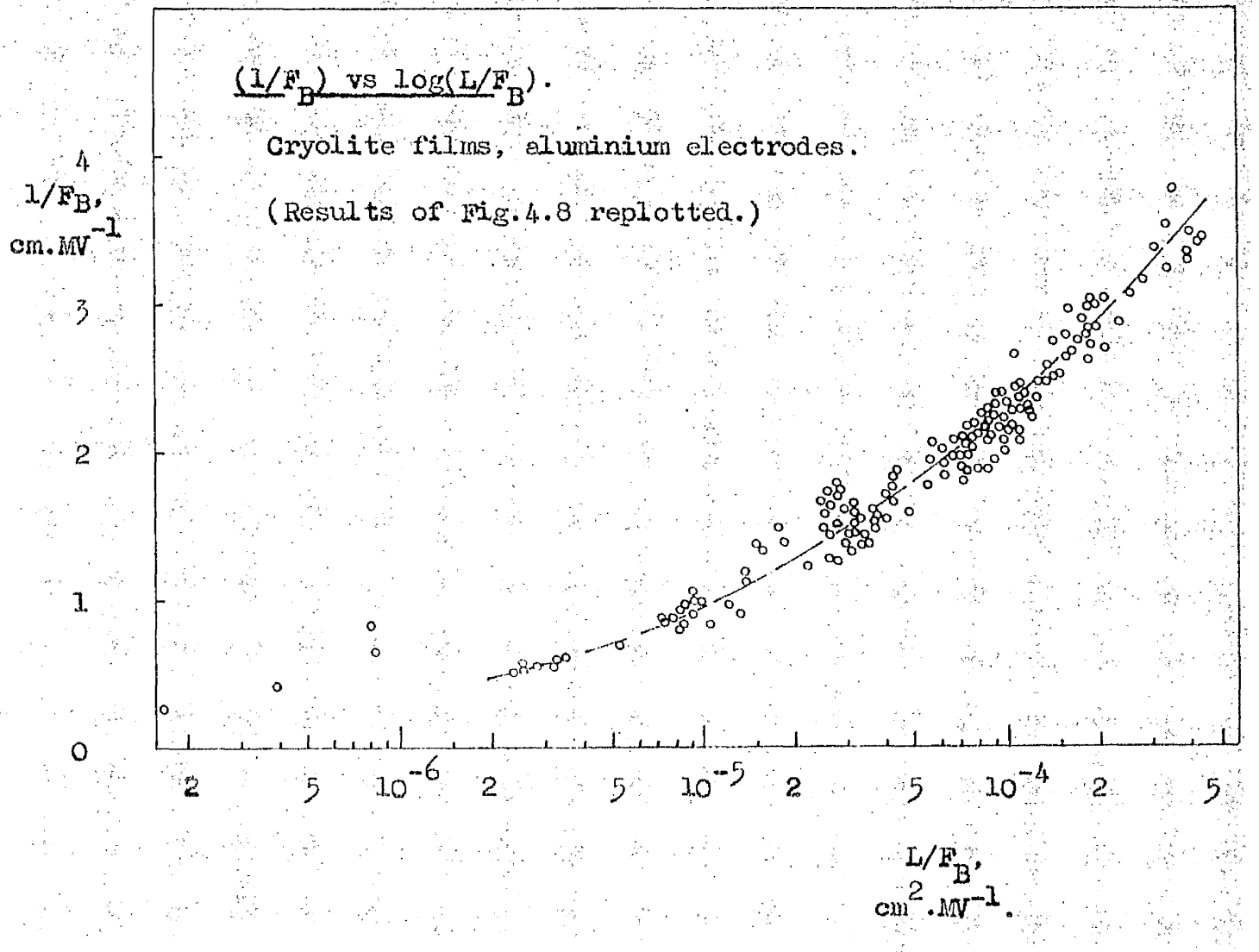

$(1/F_B)$ vs $\log(L/F_B)$.
Cryolite films, aluminium electrodes.
(Results of Fig.4.8 replotted.)
$1/F_B$, $cm.MV^{-1}$
4
3
2
1
0
2
5
10^{-6}
2
5
10^{-5}
2
5
10^{-4}
2
5
L/F_B, $cm^2.MV^{-1}$.

Fig.6.4

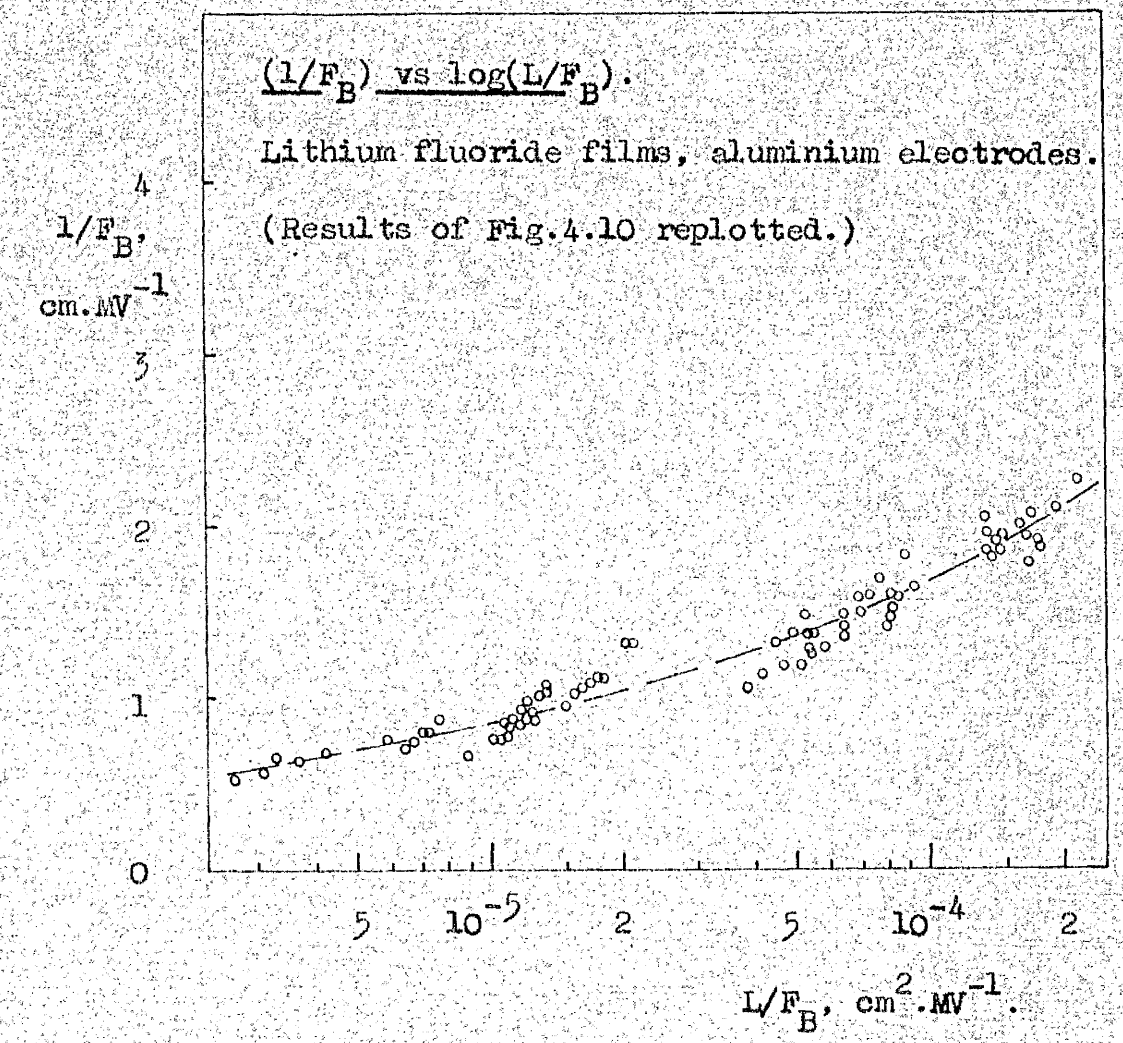

$(1/F_B)$ vs $\log(L/F_B)$.
Lithium fluoride films, aluminium electrodes.
(Results of Fig.4.10 replotted.)
$1/F_B$, cm.MV^{-1}
4
3
2
1
0
5
10^{-5}
2
5
10^{-4}
2
L/F_B, cm^2.MV^{-1}.

Fig.6.5

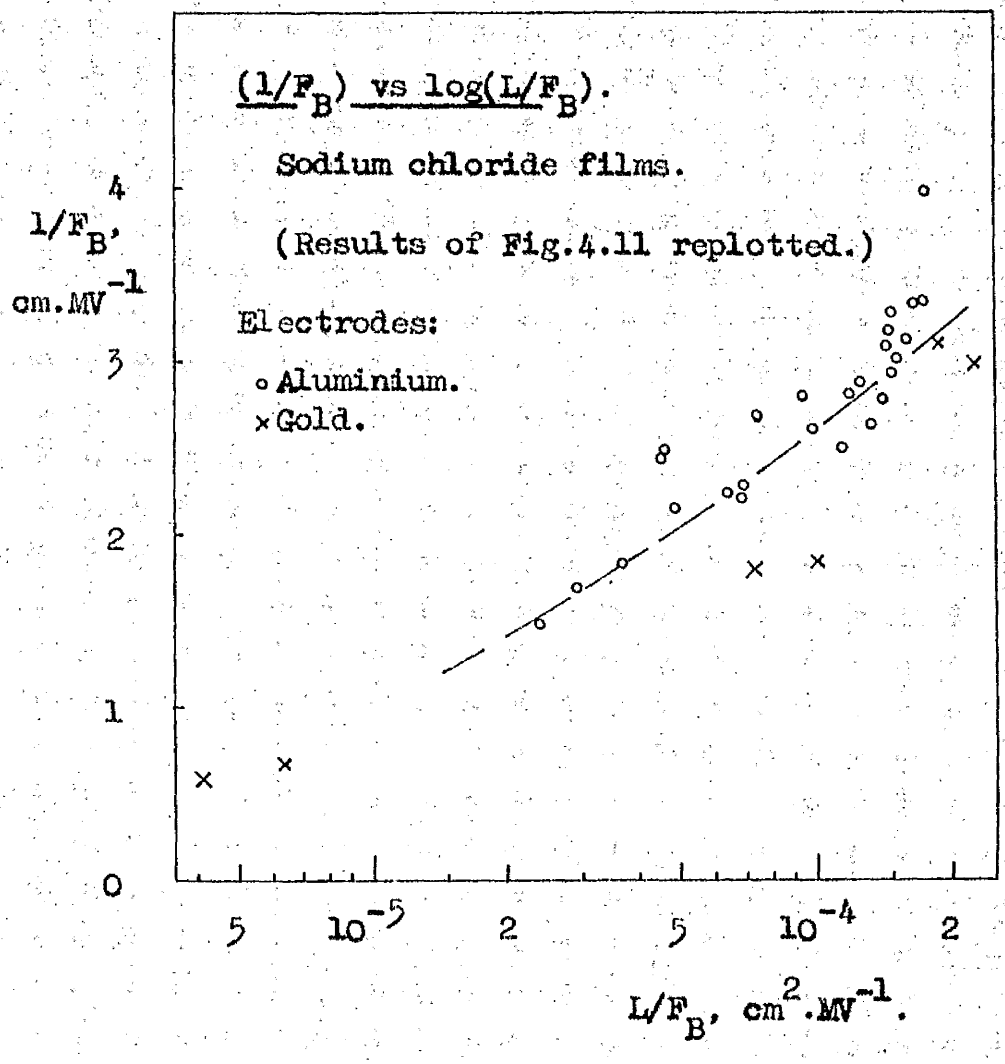

$(1/F_B)$ vs $\log(L/F_B)$.
Sodium chloride films.
(Results of Fig.4.11 replotted.)
Electrodes:
o Aluminium.
× Gold.
$1/F_B$, cm.MV^{-1}
4
3
2
1
0
5
10^{-5}
2
5
10^{-4}
2
L/F_B, cm^2.MV^{-1}.

Fig.6.6

dependence were quoted above: the Seitz-Stratton equation (2.4), and equation (1.2) which is due to Forlani and Minnaja (1964). As pointed out in Sub-section 1.3.5, a graph of $\frac{1}{F_B}$ versus log $\frac{L}{F_B}$ will be a straight line if equation (2.4) applies. The present results are shown in this form in Figs.6.4 to 6.6 and the graphs are not linear. The comparison with equation (1.2) is more promising. The equation is

$$F_B = \text{const.} L^{-\alpha}$$

with α between 0.25 and 0.5. This is quite well satisfied by the mean line of Fig.6.2, the logarithmic graph of F_B against L for lithium fluoride, with $\alpha \simeq 0.4$. This graph however extends only from 1000 Å to 10 000 Å and might show curvature outside this range. In sodium chloride (Fig.6.3) the mean gradient is about 0.6, but the exact shape of the graph is less certain and again no results are available below about 1000 Å. In Fig.6.1, the corresponding graph for cryolite, the mean gradient in the range 1000 Å to 10 000 Å is about 0.5, but at smaller thicknesses the gradient increases to about 0.9, well above the range of values of α predicted by Forlani and Minnaja. If the equation applies, this departure could be due to the fact that the thickness is beginning to approach the critical value below which avalanche breakdown theoretically cannot take place (cf. equations 2.5 and 2.6) so that a rapid increase in F_B with decreasing thickness is becoming superposed on the variation observed in thicker films, but this

suggestion/

suggestion can of course be only tentative.

In addition to the dependence of breakdown field on thickness, the results show other expected characteristics of avalanche breakdown. Firstly, the finite breakdown voltage found on extrapolating the results to small thicknesses is about 10 volts, which is of the same order as the ionisation potentials of the lattice ions. This tends to suggest a mechanism not very different from single electron avalanche breakdown, because although an applied voltage less than the ionisation potential could produce collective breakdown, Frohlich (1939) pointed out that it could not lead to breakdown by an avalanche mechanism. This evidence again cannot be taken as conclusive because of possible effects of the structure on the thickness dependence of the breakdown field, and also because the agreement is only approximate.

Secondly, the results of the tests on cryolite films at various rise rates (Fig.4.15) together with the fact that films of sodium chloride and lithium fluoride broke down at reduced applied fields when the testing voltage was increased manually, show that the breakdown field increases with the rise rate, and in this respect the results are in accordance with those of Plessner. Behaviour of this kind is often taken as indicating the existence of a time lag to breakdown (Sub-section 1.3.3). Because of the numerous possible causes of scatter in these measurements the question of distribution of time lags cannot be discussed, but the mean time lag/

lag at overvoltages less than about 10% would lie somewhere in the range 10^{-3} to 10^{-6} seconds - about the expected value for the mean time lag in avalanche breakdown. In collective breakdown, there is normally no statistical time lag and the formative time lag is probably some orders shorter.

The dependence of breakdown field on pulse duration is less likely to have been influenced by the film structure than the dependence on thickness. Other interpretations of the dependence on pulse duration are however possible. For example, if the breakdown field is being reduced by migration of any kind of space charge, one would expect a more pronounced effect at long pulse durations since there is more time for space charge to form.

There are other reasons for regarding this evidence for avalanche breakdown as tentative. Most estimates of the magnitudes of time lags to collective breakdown are deduced from theories and there are no directly obtained experimental values. Since here only a rough estimate of the magnitude is available, the statistical nature of the time lag not having been established, the possibility of collective breakdown cannot be ruled out in this way.

6.10 Possible Explanations of the Magnitude of the Breakdown Field.

If one accepts that an avalanche theory applies in bulk alkali halide single crystals, then one must in general assume that published values of electric strength have been for avalanche breakdown. It was pointed out above that another mechanism may operate/

operate in a thin film, and it could be for this reason that the breakdown field is lower. On the other hand it was shown in the last section that the breakdown mechanism is probably still of the avalanche type in thin films.

Other fundamental explanations of the low values are however possible. In a dielectric under a strong field, electrons may be freed by internal field emission, and the low breakdown fields may have been caused by migration of the negative space charge which these free electrons constitute. Ionic space charge effects are also possible, and their existence in single crystals has been confirmed by previous workers (Sub-section 1.3.1). In a freshly deposited film the number of vacancies of both signs is greatly in excess of the equilibrium value (Weaver 1962), so that conditions are ideal for a strong space charge effect. It is true that since the excess vacancies in a film will diffuse out one would expect an increase in breakdown field with time whereas the results of Fig.5.2 for lithium fluoride show no aging effect over periods of about 12 hours. However Weaver (1962) found no noticeable change in the loss tangents of lithium fluoride films over periods of the order of 24 hours, suggesting that the vacancy concentration also remained substantially constant. Ionic space charge effects must therefore be considered as a possible explanation of the low values.

Alternatively, the breakdown field of a thin film could be affected by its macrostructure. Cryolite films are known to be porous/

porous, certainly when evaporated at the pressures in the range 5×10^{-5} to 10^{-4} torr used in the present work (Bourg 1962, 1963), and probably even at pressures as low as 10^{-6} torr (Sub-section 1.2.4). Lithium fluoride films are also porous (Sub-section 1.2.3). The effective thickness of solid dielectric is lower in a porous film than in a continuous film of the same overall thickness. This would tend to increase the breakdown field. There would however be an opposing tendency for porosity to give a reduced breakdown field by causing local field concentrations. Voids in a film could also affect electronic processes in various ways. For example if electrons were accelerated through a void they would experience no collisions while within the void and would have an unusually long free path at this stage of their motion. The electrons reaching the dielectric on the side of the void nearer the anode would therefore have an increased energy, and the breakdown field would tend to be reduced. It is therefore reasonable to suggest that voids may be responsible for the low values of breakdown field.

Since thin films contain both voids and excess vacancies, the intermediate case of localised clusters of vacancies may also occur. These could provide conditions for a very strong space charge effect.

It should be noted that in all these explanations the low values are taken as being due to disorder of one kind or another. Although certain types of disorder tend to give high breakdown fields/

fields (Sub-section 1.3.2), there is nothing to indicate that other types of disorder may not tend to give low breakdown fields.

A possible criticism of these suggestions is that they fail to account for the higher values quoted by Plessner (1948) for similar thin films tested with a sphere-and-plane electrode system (Section 1.1). This difficulty might not arise since all the effects which may have been causing the low breakdown fields are to some extent localised. Space charge migration would tend to take place at the grain boundaries, where the densities of vacancies and (under a field) of free electrons would be greatest, while voids and vacancy clusters are obviously localised defects. If the area effectively covered by Plessner's spherical electrode were sufficiently small, it might not include any of these defects so that a higher applied field would be necessary for breakdown. However the author has estimated the diameter of the area as at least 0.04 mm (the calculation is given in an appendix - Section 6.12). The area is thus much too large for the difference between the present results and Plessner's to be accounted for in terms of effects localised in grain boundaries. For similar reasons one can discount any possibility that the measured breakdown fields have been low because of non-uniformities of the applied field due to the macrostructure of the metal films. The size of the aggregates in these films is known to be of the order of hundreds of angstroms (e.g. Benjamin and Weaver 1961).

Even/

Even in the case of the explanation in terms of voids or vacancy clusters, the concentration of these defects would have to be extremely low if there were to be a sufficiently low probability of finding one within an area 0.04 mm in diameter. This is readily verified by a simple calculation. The average total number N of voids in an area A of a film of thickness L is given by $vN = XLA$, where X is the void concentration and v the average volume of a void. Assuming $X = 0.05$, this gives $vN = 5 \times 10^{-12}$ cm^3 for an area 0.04 mm in diameter of a film 1000 Å thick. Thus even if the voids have an average linear dimension of the order of 1000 Å - equal to the film thickness - there will be about 5000 voids in the area. In order to explain in this way why Plessner's results are higher than those of the present author, one would clearly have to assume a void concentration X well below 1%, whereas the evidence presented in Section 1.2 suggests concentrations of the order of 10% in cryolite and lithium fluoride films. Similar considerations will apply to vacancy clusters.

It was pointed out above that after suitable treatment the breakdown field of one of the films used in this investigation may increase to approach the value to be expected on the basis of published results for single crystals, strongly suggesting that the low values are not due to extraneous effects. In any case it has been shown that none of the extraneous effects considered are likely to have led to low breakdown fields. A further possibility is suggested by the fact that a spherical metal electrode may fail to make/

make the necessary perfect contact with the dielectric surface. Small fragments of polishing abrasive could for example become embedded in the metal firmly enough not to be removed during rinsing. Alternatively, since the electrode is exposed to the residual atmosphere in the vacuum chamber throughout the routine of pumping down and depositing the films, there is a possibility of contamination of the electrode surface with diffusion pump oil. In either case breakdown might not take place unless the calculated field strength was relatively high.

6.11 The Effects of Moisture.

In Section 5.2 it was shown that the principal effect of moisture on a specimen is to lead to an increase in breakdown field by facilitating recrystallisation. Moisture does not directly cause the breakdown field to increase.

The final breakdown field after moisture has been removed was shown to depend on whether a field is present when moisture is being driven off. This was interpreted as indicating that the final crystal structure is modified by the presence of the field.

According to Mullen (1964) recrystallisation is complete in less than a second after a specimen is exposed to moisture, so that in the present work recrystallisation will have taken place at least 5 minutes before the field is applied. Thus the structural changes occurring in the presence of the field are apparently additional to those which occur on exposing the film to moisture.

The/

The effect of the applied field on the final structure could be due to some electrostatic effect such as transport of dissolved ions or some kind of orientation. This seems rather unlikely in view of the low solubility of lithium fluoride (cf. Subsection 1.2.3). On the other hand Mullen showed that heat treatment of a film led to an increase in crystallite size. Consequently the further increase in breakdown field when pulses are applied in the presence of moisture may be due to recrystallisation associated with Joule heating by conduction currents through the moist specimen.

Since Mullen found that the crystallite size of lithium fluoride films increased when moisture was admitted, the breakdown field values for specimens exposed to moisture strongly suggest that in films tested under the conditions of the present experiments a high breakdown field is associated with a large crystallite size. This is in agreement with the general conclusion that the types of disorder encountered in thin films lead to a low breakdown field and not to a high one as in previous results for bulk materials.

Finally, it may be noted that the results suggest a possible method of rendering a film electrically strong by exposing it to moisture and applying a voltage, so as to drive off the moisture in the presence of a field. The film would then be used under dry conditions. The optimum value of voltage and conditions of exposure/

exposure to moisture would be best found by trial and error for a particular layout of films on a given substrate. Alternatively, since the increase in breakdown field may be due to heating of the film, it might be possible to attain a high electric strength by baking.

6.12 Appendix: Field Strength near Plessner's Spherical Electrode

The rough calculation concerning the field strength produced in the dielectric film by a sphere-and-plane electrode system is given in this appendix since it is rather lengthy and involves no difficulties of principle.

The suggestion under discussion in Section 6.10 was that since the electric strengths of thin films might be low only at local weak spots such as voids or vacancy clusters, or grain boundaries, the area effectively covered by Plessner's spherical electrode might be so small as not to include any of these localised defects, so that a higher breakdown field would be measured by Plessner's technique. If this explanation applies then we must identify the breakdown field F_s as measured by the present technique with the breakdown field of these weak spots. Thus it is necessary to calculate the area over which the field in the dielectric exceeds F_s when the dielectric is on the verge of breakdown.

Let us assume that the deformation of the dielectric caused by the sum of the forces exerted on it by the spherical electrode as a result of the electrostatic force between the electrodes and

of/

of the elasticity of the spring supporting the metal sphere is negligible. This is not a justifiable assumption, but it will be shown below that (as already stated without proof in Section 6.10) the area calculated on this assumption is much too large to be consistent with the suggested explanation. Since the actual area over which the field exceeds F_s will be still greater, the assumption of no deformation does not affect the validity of the final conclusion.

Let us make the further assumptions that the dielectric and the metal underlayer may be regarded as infinite plane-parallel slabs, and that the dielectric and the spherical electrode make contact at a geometrical point. Let x denote radial distance measured from the point of contact. Then confining ourselves to values of x so small that the field may be regarded as perpendicular to the film surfaces, we may write for the field in the dielectric at a given value of x

$$F(x) = \frac{2RV}{2RL + \epsilon x^2} \qquad (6.4)$$

where R is the radius of the spherical electrode, V the applied voltage, L the thickness of the film, and ϵ its dielectric constant.

Let us now determine the largest value of x for which $F(x) \geq F_s$. If the field in the dielectric at the point of contact is F_p, then from (6.4) this value of x is readily shown to be/

be

$$x_M = \left[\frac{2RL}{\varepsilon} \cdot \left\{\frac{F_p}{F_s} - 1\right\}\right]^{\frac{1}{2}}, \qquad (6.5)$$

provided the assumption that the field is approximately perpendicular to the film surfaces still holds. Thus if we now identify F_p with the breakdown field as measured by Plessner, the actual field strength will exceed F_s when the dielectric is on the verge of breakdown up to a radius given by (6.5), so that x_M as so calculated is the radius of the effective area of contact. Now in Plessner's work R was $\frac{1}{16}$ in. or approximately 0.15 cm. Since F_p is approximately equal to the bulk breakdown field, F_p/F_s will be about 10 and we may take $(F_p/F_s) - 1 = 10$. A typical value for ε is 5. Substituting these values in equation (6.5) and taking L = 1000 Å gives $x_M = 0.02$ mm. In fact x_M will be larger as a result of deformation of the dielectric. Thus the statement in Section 6.10 that the field in the dielectric exceeds F_s over an area at least 0.04 mm in diameter is justified.

It remains only to consider the validity of the assumption that the lines of force are perpendicular to the film surfaces. The thickness of the air film between the dielectric and the spherical electrode is $y = \frac{x^2}{2R}$. At x = 0.02 mm, this gives $y = 3 \times 10^{-5}$ cm $= 2 \times 10^{-4}$ R. y is thus negligible in comparison with the radius of the sphere and the assumption is valid to an ample degree of approximation for the present calculation.

CHAPTER 7

CONCLUSIONS

7.1. The Magnitude of the Breakdown Field: Thin Film and Bulk Breakdown.

Comparison of the present values of breakdown field for thin films of sodium chloride and lithium fluoride between evaporated metal electrodes with previous values for single crystals of the same materials (Section 6.1) confirms Weaver's preliminary conclusion (Section 1.1) that evaporated films break down at lower applied fields than single crystals of the same material, and shows that the breakdown field of a thin film is about an order of magnitude below the expected value for a single crystal specimen of the same thickness. However after exposure to moisture the breakdown field of a film may increase to approach the single-crystal value (Section 5.2). The low values are therefore apparently not due to unwanted effects. In any case possible side effects were considered in Section 6.2 to 6.8 and it was shown that none of them are likely to have led to low breakdown fields.

In Section 6.10 it was suggested that the breakdown fields may have been low because of space charge migration. The space charge concerned could have consisted of ions migrating by a vacancy mechanism, or of electrons emitted by the applied field from the numerous potential wells. An alternative explanation suggested was that voids in the films might have caused the low values/

values by producing local field concentrations and by directly affecting the passage of the breakdown electrons through the dielectric.

Whatever the detailed explanation, the results strongly suggest that although in single crystals of alkali halides a disordered structure leads to a high breakdown field (Subsection 1.3.2), the types of disorder occurring in thin films may lead to a reduced value.

7.2 The Breakdown Mechanism.

Various aspects of the results tend to indicate that breakdown is of the avalanche type. The increase in breakdown field with decreasing thickness is the strongest piece of evidence. It is valid on the assumption that the factor by which the breakdown field is reduced is independent of thickness. The existence of a finite voltage of the same order as the ionisation potential of a negative lattice ion also tends to indicate an avalanche mechanism.

The fact that the breakdown field increases as the duration of the applied voltage is reduced could be due to a time lag somewhere in the range 10^{-3} to 10^{-6} seconds and is therefore consistent with the suggestion of an avalanche mechanism. However the variation could also be due to space charge migration. In any case merely to show that a time lag of this order exists is not sufficient to establish that avalanche breakdown is taking place/

place (Sub-section 1.3.3). The difficulties of interpretation were discussed in detail in Section 6.9.

7.3 The Effects of Moisture.

In Section 5.2 it was shown that the breakdown field of a lithium fluoride film exposed to air saturated with water vapour is greater when the film is tested while still in its moist environment than when it is tested after being dried by being kept under vacuum. Both values of breakdown field are greater than the value for a freshly deposited film tested under vacuum. No effects of aging lithium fluoride films (under either dry or moist conditions) for periods of the order of those involved in carrying out the experiments were observed. Three possible interpretations were suggested in Section 5.2:

(a) The increase in breakdown field is purely and directly due to the presence of adsorbed moisture. Some moisture is still present even on the films dried under vacuum, but more is present on the films tested under moist conditions. The breakdown field is thus increased in the specimens tested after being dried under vacuum, but is still higher in those tested in the presence of moisture.

(b) The increase observed in the specimens tested after drying under vacuum is due to recrystallisation of the dielectric. The further increase in the specimens tested under moist conditions is directly due to the moisture.

(c)/

(c) The increase is entirely due to recrystallisation, moisture having little or no direct effect. The recrystallisation process is in some way modified by the presence of the field so as to give the further increase in the specimens tested under moist conditions.

However when specimens were exposed to voltage pulses in the presence of moisture until they were on the verge of breakdown and then tested after being kept in vacuum for at least an hour, their breakdown voltages had a mean value greater than the mean breakdown voltage for specimens exposed to moisture and tested while still under moist conditions. In some cases the breakdown field approached the expected single-crystal value. This strongly suggests interpretation (c): the increase in breakdown field seems to be due entirely to recrystallisation in the presence of moisture. No detailed explanation of the very high values observed in this last group of specimens has however been offered.

It was tentatively suggested in Section 6.11 that the effect on the recrystallisation process of applying a field may be due to Joule heating. It was also pointed out that since this process involves an increase in crystallite size, i.e. a transition to a more ordered structure, the results for specimens exposed to water vapour are consistent with the suggestion that the types of disorder encountered in thin films lead to a low breakdown field. It is not however possible to discuss the exact means by which recrystallisation affects the breakdown field.

Some/

Some indications were obtained that the breakdown field increases on exposure to moisture in cryolite as well as lithium fluoride (Section 5.3).

7.4 Effects of the Electrode Metal.

The breakdown fields are in general not seriously affected by the electrodes. Since the results obtained did not depend on whether the electrodes were of gold or aluminium, it may be concluded that oxide layers on the aluminium do not affect the breakdown fields measured (Section 4.2). Moreover since the same values of breakdown field were obtained with cathodes of silver, aluminium, and gold, it appears that the breakdown field does not depend on the cathode work function. This however is a preliminary conclusion because these three metals do not differ greatly in their work functions. Internal fields caused by using electrodes of dissimilar metals would be too small to affect the present results measurably (Section 4.2).

Silver seemed to behave anomalously as an anode metal (Section 4.2). When it was used the measured breakdown voltage was reduced, the relative frequency of initial short circuits was increased, and self-healing of the electrodes (Sections 4.1 and 4.2) seldom occurred. These effects were attributed to migration of Ag^+ ions under the action of the applied field. Apart from the behaviour of silver anodes, no effects of the electrode material were detected.

7.5 Further Work./

7.5 Further Work

One of the principal conclusions summarised in the foregoing sections was that the types of disorder found in thin films may lead to low breakdown fields. Further information on the effects of disorder might be obtained by using films with a more ordered structure than films deposited on to glass at room temperature as in the present work. Epitaxially grown films would ideally be used, but even films condensed on heated glass substrates are known to have a relatively ordered structure (e.g. Mullen 1964) and might well be useful. If films of these types were found to have higher breakdown fields than the films studied in the present investigation, the conclusion would be confirmed. Moreover if this were observed and if the thickness dependence of the breakdown field continued essentially unchanged, the evidence for avalanche breakdown would be strengthened.

Another way of obtaining information on the breakdown mechanism would be to study time lags to breakdown. Some evidence along these lines has already been obtained by investigating the dependence of breakdown field on applied voltage duration (Sections 4.4, 6.9, and 7.2), but this evidence was not conclusive and it would be more satisfactory to attempt to confirm the existence of a statistical time lag by direct measurement and to find whether the distribution of time lags was in accordance with the theoretical equation.

Interesting results on several aspects of thin film breakdown might/

might be obtained by testing specimens after aging them for longer periods or at higher temperatures than those already studied. An increase in breakdown field on aging would tend to confirm the correlation between disorder and a low breakdown field. The use of specimens heated under moist as well as dry conditions could well be useful in finding whether the additional increase in breakdown field, observed when the specimens are dried by applying voltage pulses to them rather than by keeping them in vacuum, is due to Joule heating and in what respects the presence of moisture is necessary. This could have practical applications in developing a method of rendering films electrically strong as already discussed in Section 6.11.

AUSTEN, A.E.W., and WHITEHEAD, S., 1940, Proc. Roy. Soc. A 176, 33.

BALYGIN, I.E., 1960, Fiz. Tverdogo Tela 2, 1723 (Soviet Phys. - Solid State 2, 1583, 1961).

BAUER, E., 1956, Z. Kristallogr. 107, 72, 265, and 290.

BENJAMIN, P., and WEAVER, C., 1961, Proc. Roy. Soc. A 261, 516.

BLACKBURN, H., and CAMPBELL, D.S., 1963, Phil. Mag. (8th Ser.) 8, 823.

BOER, K.W., DZESIATY, J., KUMMEL, U., and MISSELWITZ, W., 1962, Physica Status Solidi 2, 48.

BOURG, M., 1962, Optica Acta 9, 177; Rev. Opt. 41, 165 and 175; 1963, J. de Phys. 24, 162.

BOUSQUET, P., 1955, Comptes Rendus (Paris) 240, 2502; ibid. 241, 478.

BROWN, L.C., 1961, Ph.D. Thesis, University of Glasgow.

BUEHL, R.C., and von HIPPEL, A., 1939, Phys. Rev. 56, 941.

CALDERWOOD, J.H., COOPER, R., and WALLACE, A.A., 1952, Proc. Phys. Soc. B 65, 301; 1953, Proc. I.E.E. 100, Pt. 2A, 105.

CALLEN, H.B., 1949, Phys. Rev. 76, 1394.

CHYNOWETH, A.G., and McKAY, K.G., 1957, Phys. Rev. 108, 29.

COLLINGS, P.R., and HIRSCH, J., 1964, Brit. J. App. Phys. 15, 797.

COOPER, R., 1962, Prog. Dielectrics 5, 95.

COOPER, R., and FERNANDEZ, A., 1958, Proc. Phys. Soc. 71, 688.

COOPER, R., and GROSSART, D.T., 1956, Proc. Phys. Soc. B 69, 1351.

COOPER/

COOPER, R., HIGGIN, R.M., and SMITH, W.A., 1960, Proc. Phys. Soc. 76, 817.

COOPER, R., and SMITH, W.A., 1961, Proc. Phys. Soc. 78, 734.

COOPER, R., and WALLACE, A.A., 1953, Proc. Phys. Soc. B 66, 1113; 1956, ibid. B 69, 1287.

DAVISSON, J.W., 1959, Prog. Dielectrics 1, 59.

FISHER, R.A., and YATES, F., 1957, "Statistical Tables for Biological, Agricultural, and Medical Research" (Oliver and Boyd, Edinburgh).

FORLANI, F., and MINNAJA, N., 1964, Physica Status Solidi 4, 311.

FRANZ, W., 1952, Z. Phys. 132, 285; 1956, Encyclopaedia of Physics (Springer, Berlin).

FROHLICH, H., 1937, Proc. Roy. Soc. A 160, 230; 1939, ibid. A 172, 94; 1947a, ibid. A 188, 521; 1947b, ibid. A 188, 532.

FROHLICH, H., and MOTT, N.F., 1939, Proc. Roy. Soc. A 171, 496.

FROHLICH, H., and PARANJAPE, B.V., 1956, Proc. Phys. Soc. B 69, 21 and 866.

GUNTHERSCHULTZE, A., 1923, Phys. Z. 24, 212.

HALLIDAY, J.S., RYMER, T.B., and WRIGHT, K.H.R., 1954, Proc. Roy. Soc. A 225, 548.

"Handbook of Chemistry and Physics", 43rd edn., 1961 - 62 (Chemical Rubber Publishing Co., Cleveland, Ohio), p.2594.

HAWORTH, F.E., and BOZORTH, R.M., 1934, Physics 5, 15.

HEAVENS, O.S., 1955, "Optical Properties of Thin Solid Films" (Butterworth, London); 1960, Rep. Prog. Phys. 23, 1.

HEAVENS/

HEAVENS, O.S., and SMITH, S.D., 1957, J. Opt. Soc. Amer. 47, 469.

HELLER, W.R., 1951, Phys. Rev. 84, 1130.

HOFFMAN, R.W., DANIELS, R.D., and CRITTENDEN, E.C., 1954, Proc. Phys. Soc. B 67, 497.

HOFSTADTER, R., 1949, Nucleonics 4, No.4, p.2.

HOLLAND, L., 1953, J. Opt. Soc. Amer. 43, 376; 1956, "Vacuum Deposition of Thin Films" (Chapman and Hall, London); 1958, Brit. J. App. Phys. 9, 410.

INUISHI, Y., and SUITA, T., 1952, J. Phys. Soc. Japan 7, 641; 1953, ibid. 8, 567; 1954, ibid 9, 431; 1955a, ibid. 10, 588; 1955b, ibid. 10, 590.

KAWAMURA, H., and AZUMA, K., 1953, J. Phys. Soc. Japan 8, 797.

KAWAMURA, H., OHKURA, H., and KIKUCHI, T., 1954, J. Phys. Soc. Japan 9, 541.

KAWAMURA, H., and ONUKI, M., 1952, J. Phys. Soc. Japan 7, 121.

KOENIG, H., and HELWIG, G., 1950, Optik 6, 111.

KOHMAN, G.T., HERMANCE, H.W., and DONNES, G.H., 1955, Bell Sys. Tech. J. 34, 1115.

KONOROVA, E.A., and SOROKINA, L.A., 1957, Zh. Eksper. Teor. Fiz. 32, 143 (Soviet Phys. - JETP 5, 143).

KOPPELMANN, G., KREBS, K., and LEYENDECKER, L., 1961, Z. Phys. 163, 557.

KOSTRYGIN, V.A., 1960, Fiz. Tverdogo Tela 2, 1841 (Soviet Phys. - Solid State 2, 1664).

KUCHIN/

KUCHIN, V.D., 1959, Fiz. Tverdogo Tela 1, 450 (Soviety Phys. - Solid State 1, 406).

LOMER, P.D., 1950, Nature 166, 191; Proc. Phys. Soc. B 63, 813.

MACFARLANE, J.C., 1964, Ph.D. Thesis, University of Glasgow; Final Report, Ministry of Aviation Contract No. PD/65/05 (University of Strathclyde).

MASON, J.H., 1959, Prog. Dielectrics 1, 1.

MEL'NIKOV, M.A., 1959, Zh. Eksper. Teor. Fiz. 36, 613 (Soviet Phys. - JETP 9, 425).

MERRILL, R.C., and WEST, R.A., 1963, Spring Meeting, Electrochem. Soc., Pittsburgh.

MULLEN, D.C., 1964, Final Report, Ministry of Aviation Contract No. PD/65/04 (University of Strathclyde).

O'DWYER, J.J., 1958, Adv. Phys. 7, 349.

PLESSNER, K.W., 1948, Proc. Phys. Soc. 60, 243.

POWERS, D.A., and SUITA, T., 1955, J. App. Phys. 26, 1244.

RAMOS, F., and WILMAN, H., 1962, Anal. Real Soc. Espan. Fis. Quim. A 58, 51.

RYU, I., and KAWAMURA, H., 1954, J. Phys. Soc. Japan 9, 438.

SAITO, Y., 1936, J.I.E.E. Japan 56, 1036.

SCHULZ, L.G., 1949, J. Chem. Phys. 17, 1153.

SCHULZ, L.G., and SCHEIBNER, E.J., 1950, J. Opt. Soc. Amer. 40, 761.

SEITZ, F., 1946, Rev. Mod. Phys. 18, 384; 1948, Phys. Rev. 73, 549; 1949. Phys. Rev. 76, 1376; 1954, Rev. Mod. Phys. 26, 7.

SENNETT, R.S., and SCOTT, G.D., 1950, J. Opt. Soc. Amer. 40, 203.

SIDDALL, G., 1959 - 60, Vacuum 9, 274.

SIMMONS, J.G., 1963, Phys. Rev. Letters 10, 10.

SONCHIK, K.K., 1957, Zh. Eksper. Teor. Fiz. 33, 1303 (Soviet Phys. - JETP 6, 1003, 1958); 1958a, Dokl. Akad. Nauk SSSR 123, 76; 1958b, Izv. Akad. Nauk. SSSR (Ser. Fiz.) 22, 423.

STRATTON, R., 1961, Prog. Dielectrics 3, 233.

TOLANSKY, S., 1948, "Multiple-Beam Interferometry of Surfaces and Films" (Clarendon Press, Oxford).

VEELKEN, R., 1955, Z. Phys. 142, 476 and 544.

von HIPPEL, A., 1931a, Z. Phys. 67, 707; 1931b, Z. Phys. 68, 309; 1932, Z. Phys. 75, 145; 1934, Z. Phys. 88, 358; 1935, Ergebn. Exakt. Naturw. 14, 79; 1937, J. App. Phys. 8, 815; 1954, "Dielectrics and Waves" (Wiley, New York).

von HIPPEL, A., and ALGER, R.S., 1949, Phys. Rev. 76, 127.

von HIPPEL, A., GROSS, E.P., JELATIS, J.G., and GELLER, M., 1953, Phys. Rev. 91, 568.

VOROB'EV, A.A., 1956, Zh. Tekh. Fiz. 26, 327 (Soviet Phys. - Tech. Phys. 1, 322).

VOROB'EV, A.A., and VOROB'EV, G.A., 1958a, Izv. Akad. Nauk SSSR (Ser. Fiz.) 22, 392; 1958b, ibid. 22, 397.

VOROB'EV, A.A., VOROB'EV, G.A., and MEL'NIKOV, M.A., 1960, Fiz. Tverdogo Tela 2, 2019 (Soviet Phys. - Solid State 2, 1814).

VOROB'EV, G.A., 1956, Zh. Eksper. Teor. Fiz. 30, 256 (Soviet Phys. - JETP 3, 225); 1962, Fiz. Tverdogo Tela 4, 1363 (Soviet Phys./

Phys. - Solid State 4, 1001).

VOROB'EV, G.A., and KOSTRYGIN, V.A., 1962, Fiz. Tverdogo Tela 4, 811 (Soviet Phys. - Solid State 4, 595).

WEAVER, C., 1962, Adv. Phys. 11, 83.

WHITEHEAD, S., 1951, "Dielectric Breakdown of Solids" (Clarendon Press, Oxford).

WILLIAMS, R., 1962, Phys. Rev. 125, 850.

YAMANAKA, C., and SUITA, T., 1952, J. Phys. Soc. Japan 7, 225.

ZAVADOVSKAYA, E.K., 1951, Dokl. Akad. Nauk SSSR 81, 541.

ZENER, C., 1934, Proc. Roy. Soc. A 145, 523.